THERMODYNAMIC PROPERTIES OF $CaO-Al_2O_3-SiO_2$ SLAGS.

THESIS

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by

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CHAPTER I.

INTRODUCTION.

INTRODUCTION.

The manufacture of iron and steel was well established as an art long before any major scientific investigations were carried out on the reactions underlying the processes. Over the last thirty years, research has discovered much about the fundamentals of the processes and the results obtained are now being used in iron- and steel-making plants as means of controlling rather complex operations.

The important part played by the slag phase in these operations has long been recognised. In iron-making the quality of the iron produced, which depends mainly on the sulphur and silicon contents, is determined by reactions which take place between the metal and slag phases. In steel making, slag-metal reactions play a major role in the removal of silicon, phosphorus, carbon and sulphur, although gas-metal and gas-slag reactions may also occur, especially in the cases of desulphurisation and decarbonisation.

It is obvious that, before the reactions governing the iron- and steel-making processes can be fully understood, a knowledge of the constitution of the liquid slag phase is necessary. The present knowledge of the constitution of iron- and steel-making has been derived from various works and laboratory investigations, the most fruitful source as yet being the investigation of slag-metal equilibria. However, such data are not easy to interpret, on account of the lack of information on the activity coefficients of various constituents in both the liquid iron and the liquid slag phases.

In the present approach to the problem of liquid slag constitution it was decided to study slag-gas equilibria. The information gained from such studies is usually easier to interpret than that obtained from slag-metal studies, since the gas phase can be regarded as an ideal solution and the activity or potential of each component is therefore obtained from a knowledge of the equilibrium conditions at the temperature of study. The iron oxide-oxygen equilibrium has already been studied by White(1), by Darken and Gurry(2) and by Chipman and Larson(3), but the knowledge of slag constitution thus obtained was limited to slags containing iron oxides and other oxides which combine with the iron oxides. In the present work, the equilibrium between molten slags and gases containing sulphur has been studied. This can give information not only about the constitution of liquid slags used in iron- and steel-making, and the activities of the slag components, but also about the transfer of sulphur between gas and slag in the open-hearth steelmaking process.

The ultimate reaction to be studied is

$$\tfrac{1}{2} S_2 + O^{--} = \tfrac{1}{2} O_2 + S^{--}$$

Since the number of variables involved in using iron- and steel-making slags and gases would have been too great to cope with under laboratory conditions, the slag systems studied were limited to those containing CaO as the only basic oxide constituent, and Al_2O_3 or SiO_2 or both as the acidic oxide constituents, while the gases used were mixtures of CO, CO_2 and SO_2, the simplest possible to give calculable values of P_{O_2} and P_{S_2} The present work was almost completely limited to an experimental temperature of 1500°C.

CHAPTER II.

REVIEW OF PREVIOUS WORK.

The earliest attempts to apply the laws of physical chemistry to iron- and steel-making slag-metal reaction used the total concentrations of the reactants, but met with little success. Consequently attempts were made to assess the "free" concentrations of the reactants in the slag, i.e., that part of the "total" concentration of a component which can be regarded as available for chemical reaction. The assumption was made that the compounds found in the solidified slags were also present in the liquid state and that these compounds were partially dissociated in the liquid slag. Thus Schenck(4) assumed that the compounds formed in a steel-making slag were $CaO.SiO_2$, $2MnO.SiO_2$, $2FeO.SiO_2$, $3CaO.P_2O_5$ or $4CaO.P_2O_5$, and $3CaO.Fe_3O_4$, and that they were in equilibrium with the "free" concentrations of their component oxides, e.g.,

$$2FeO.SiO_2 = 2FeO + SiO_2$$

From a large amount of works data on slag-metal relationships and from the laboratory results of Korber and Oelsen(5), Schenck obtained values for the dissociation constants of these compounds, and constructed charts relating the free concentrations of slag components to the chemical analysis of the slag. Considering the assumptions involved in Schenck's treatment, the agreement obtained by various workers between observed steelmaking data and values calculated from Schenck's charts is good, although it is by no means perfect.

White(1) obtained dissociation constants for compounds formed between iron oxides, silica and lime, by comparing the loss in weight caused by the dissociation of Fe_2O_3, when melted alone, with the loss observed on the addition of known quantities of silica and lime,

separately and together. White attributed the change in dissociation to the formation of ferrous silicates and calcium ferrites and calculated dissociation constants for these compounds in a manner similar to that of Schenck. The agreement between the results of Schenck and of White is not good, but, since White's experiments were carried out in the absence of molten iron and at oxygen pressures of 2-76 cms., this is not really surprising.

Recently, Grant and Chipman(6), investigating sulphur equilibria between liquid iron and slags, explained their results on the basis of a slag constitution model similar to that of Schenck. The basic oxides, CaO, MgO and MnO, were taken to be equivalent, on a molar basis, in their capacities to neutralise the acidic oxides, and were taken to combine with them according to the following rules.

2 Base : $1SiO_2$, 4 Base : $1P_2O_5$; 2 Base : $1Al_2O_3$, 1 Base : $1Fe_2O_3$, the remaining base being termed "excess base". Their results showed that the sulphur distribution ratio, (S)/[S], was controlled by the excess base or acid count, and that the relationship was almost linear.

Theories based on the ionic concept of slag constitution have been put forward by Herasymenko(7), Temkin(8), Kheinman(9) and Flood, Førland and Grjotheim(10) to explain slag-metal equilibria. Herasymenko's theory assumed complete ionisation of the slag, and gave reasonable agreement with acid open-hearth data. It was modified in a later paper(11) to explain basic steelmaking reactions, but the "equilibrium constants" were found to vary with slag composition. This was not surprising, since slag concentrations were expressed as ion fractions, i.e., the

number of gm. ions of the ion considered divided by the total number of gm. ions present (cations and anions) and constancy of the "equilibrium constant" would have implied that the ions were randomly mixed irrespective of their nature or the sign of their charge.

The theory put forward by Temkin(8) was similar to that of Herasymenko, but differed in one important respect, in that it assumed that each cation was surrounded by anions and vice versa. Kheinman(9) pointed out that the concept of non-ionised oxides and compounds put forward by Schenck(4) could be used to explain oxygen distribution but not sulphur distribution between metal and basic slags, whereas the ionic theory of Temkin could explain sulphur distribution but not oxygen distribution, and suggested that both sulphur and oxygen distribution could be accounted for satisfactorily if it were assumed that silicate melts contained both ionised and non-ionised compounds.

It is unlikely, however, that the various cations are associated equally with the different anions present, irrespective of charge, size, co-ordination number, etc., as is implicit in Temkin's theory. Flood, Førland and Grjotheim(10) made allowance for the differences in the energies of interaction of the various ions present and achieved considerable success in the interpretation of sulphur, manganese and phosphorus equilibria under basic slags.

Less success has been achieved in the application of these theories to acid steelmaking, principally because of the lack of knowledge of the state of combination of silica in acid slags. Thus before the ionic theory could be applied it would be necessary to know the types of silicate ions present in acid slags.

The purely thermodynamic approach to the problem of slag-constitution, in which the chemical activity of each component is utilized in the evaluation of slag-metal equilibria, is more useful than an approach relying on one of the theories given above, since it can be used independently of the methods and assumptions involved in obtaining the activity values. Thus the attempts which workers such as Schenck and Chipman have made to obtain suitable expressions for the "free" concentrations of slag reactants in slag-metal reactions can be regarded as methods of assessing the activity of those reactants in slags. In recent years, Richardson(12) has used thermodynamic data to estimate the activity of FeO and SiO_2 in molten FeO-SiO_2 slags; Rey(13) has used the phase diagrams of a number of binary silicate systems to estimate the activities of SiO_2 and the corresponding metal oxides; and Bell, Murad and Carter(14) have used the results of experiments on the distribution of Mn and O between iron and FeO-MnO-SiO_2 slags to determine activities of the oxide components of these slags. Such activity values can be used in the evaluation of slag-metal equilibria independently of how they were obtained. The present approach, through gas-slag equilibria would fall to be included in this category.

The amount of data at present available on reactions of the slag phase with the furnace atmosphere is small compared with the data available on slag-metal reactions, and hence there is not an adequate basis for a full understanding of the transfer mechanism of sulphur and oxygen between gas and slag. Apart from the recent work of Fincham and Richardson(15) information obtained by laboratory investigations has been confined to

studies on oxygen transfer between the gas phase and slags containing iron oxides, and information on gas-slag sulphur transfer has been obtained only from works data and sulphur balances, which are, of course, unsatisfactory as sources of fundamental data on iron- and steel-making reactions.

Laboratory investigations on oxygen-iron oxide gas-slag equilibria have been mainly of two types:-

(a) the study of the dissociation of molten slags in an evacuated system, the oxygen pressure resulting from its decomposition being measured, and

(b) the study of the equilibration of slags with gases of known oxygen potentials.

The former method was used by Krings and Schackmann(16) in their studies of the dissociation of iron oxide-lime-silica mixtures at temperatures of 1550-1600°C. The latter method was first used by White(1), as outlined above. The decomposition of ferric oxide into oxygen and lower iron oxides was studied at various temperatures under oxygen pressures of 2 - 76 cms. and the effect of additions of CaO and SiO_2 upon this dissociation was also observed. The experimental procedure involved suspending a sample in a platinum crucible from one arm of an analytical balance, the proportions of ferric and ferrous oxides being calculated from observations of the weight loss caused by the reaction

$$Fe_2O_3 = 2FeO + \tfrac{1}{2}O_2$$

Unfortunately iron dissolves in the crucible according to the reaction

$$FeO = Fe\ (\text{in Pt}) + \tfrac{1}{2}O_2$$

thus causing a permanent weight loss to the system. Reviewing this work, Larson and Chipman(3) indicated that White's results do not agree with the later work of Darken and Gurry(2) on account of a faulty method of correcting for this reaction.

Darken and Gurry(2) worked on the iron-oxygen system melting iron oxide in a platinum crucible under an atmosphere of controlled oxygen potential. Depending upon the oxygen potential desired, their atmospheres were obtained from $CO-CO_2$, CO_2-H_2, H_2O, CO_2, air or O_2, gases. By calculations from the ferrous and ferric oxide analyses of the quenched samples, Darken and Gurry were able to determine the iron and oxygen activities in the various slags used. In subsequent work they investigated the effect of additions of CaO, MnO and SiO_2 on the iron and oxygen activities.

Analogous methods of slag-gas equilibria using $CO-CO_2$ gas mixtures to fix the oxygen potentials of the gases, have been employed by Schuhmann and Ensio(17) and by Michal and Schuhmann(18) in studies of the thermodynamic properties of iron silicate slags. Thus the laboratory technique involved in slag-gas equilibria investigations of oxygen transfer requires

(a) the use of a suitable gas mixture to give the desired oxygen potential at the experimental temperature, and

(b) satisfactory techniques for the freezing of the equilibrium and the subsequent analysis of the sample.

Both of these conditions were readily obtainable in the above investigations of oxygen-iron oxide equilibria, and it follows that similar

conditions would be necessary for the investigation of gas-slag sulphur transfer.

The only work which has been carried out on gas-slag equilibria involving sulphur transfer is that of Fincham and Richardson(15) which was published when the present work was almost completed. Their work was carried out using a similar experimental technique to that employed in the present work. They investigated the absorption of sulphur by various molten silicates and aluminates and iron- and steel-making slags. Small samples of the slags were brought into equilibrium with gas mixtures of CO_2, H_2, SO_2 and N_2 in such proportions as to give, at the experimental temperatures the required oxygen and sulphur potentials as calculated from the available thermodynamic data. Whereas in the present work a detailed study was made of the $CaO-Al_2O_3-SiO_2$ system at 1500°C, over sixty slag compositions being used, Fincham and Richardson investigated only a few $CaO-Al_2O_3-SiO_2$ slag compositions, one $MgO-SiO_2$ slag, two $FeO-SiO_2$ slags. On the other hand, Fincham and Richardson made a detailed investigation of the effect of temperature and the oxygen potential of the gas phases. Their work was carried out at four temperatures ranging from 1425-1650°C, and at oxygen potentials from $1 - 10^{-11}$ atmospheres. From their work, Fincham and Richardson were able to compare the relative sulphide capacities of the slags investigated, within the temperature range important in iron- and steel-making, and certain comparisons will be made between the results of the present work and their results.

It was stated in the introduction that a study of gas-slag

equilibria involving sulphur transfer would give information about the desulphurisation process in steelmaking. It is, therefore, desirable to note here some of the results obtained from works data and sulphur balances which bear on the problem of desulphurisation, noting especially those pertaining to gas-slag equilibria.

Whiteley(19) with data from an acid open-hearth furnace, was one of the first to study the effect of the sulphur content of the furnace gases on the desulphurisation of the bath. He found that, during the refining period, sulphur was picked up by the bath only when the gas was incompletely burnt. With completely burnt gas, a slight loss of sulphur from the bath to the gas could occur.

Schenck(4) in another early study of works data investigated the sulphurisation and desulphurisation of the molten bath by the heating gases during the boil, and concluded that the reaction takes place mainly between the gas and the slag, while the metal bath is subject to the influence of the gaseous phase by way of the slag. Schenck assumed that the sulphur in the gas is present almost entirely as SO_2, and reacts with the free lime according to the equation

$$SO_2 + CaO + 3CO = CaS + 3CO_2$$

He concluded that sulphurisation of the bath is encouraged by reducing conditions.

Herty et al(20), stated that, once the slag has covered the bath in the basic open-hearth furnace, transfer of sulphur from gas to slag takes place according to the following reactions.

$$SO_2 + CaO + 3CO = CaS + 3CO_2,$$

the CO being derived from the carbon-oxygen reaction in the bath, and

$$SO_2 + CaO + 3Fe_{(l)} = CaS + 3FeO,$$

the iron being present as small droplets suspended in the slag. Assuming that all the sulphur in the gas is present as SO_2, Herty worked out the ratio

$$\frac{\text{Vol \% sulphur in the gas over the bath}}{\text{\% sulphur in the slag}} = 0{\cdot}27$$

but this ratio has no thermodynamic significance since neither the CO/CO_2 ratio of the gas, nor the state of oxidation of the slag, nor the effect of temperature has been taken into account.

Chipman and Ta Li(21) in their investigations into the problem, also emphasised the importance of the slag phase in desulphurisation. They showed that the most important variable in desulphurisation is the free lime content of the slag, and that oxygen tends to desulphurise the slag by oxidising CaS to SO_2. However, as other substances in the slag are competing with the CaS for the small amount of oxygen available, there could be no efficient desulphurisation via the excess air in the flame.

At various times, investigators have endeavoured to obtain an overall picture of the movement of sulphur in an open-hearth heat by carrying out a sulphur balance over the whole operation. Due to the practical difficulties encountered in carrying out such a test, and the large number of personnel required to carry out the necessary work, relatively few complete sulphur balances have been carried out. Such balances as have been carried out furnish us with information on gas-slag

sulphur movement as follows. Eisenstecken and Schultz(22) showed that in the heats they investigated in a furnace fired by a mixture of coke-oven gas and blast furnace gas, the sulphur in the gas was only absorbed in the charging and melting periods and that not only was this sulphur completely liberated in the boil during the refining period, but the bath underwent a net loss of sulphur. This desulphurisation was found to take place independently of whether a reducing or oxidising atmosphere was present.

Short and Meyrick(23) in a similar sulphur balance on a furnace fired by a mixture of coke-oven gas and producer gas, pointed out that by far the greatest amount of sulphur entering and leaving the furnace does so with the gas. Inthis test a little more sulphur was found to leave the furnace with the waste gases than enter with the fuel gases. Hence Short and Meyrick's results are in conformity with the observations of Eisenstecken and Schultz, since desulphurisation of the charge has taken place. Short and Meyrick also found that the use of sulphur-free instead of sulphur-containing gases has very little effect on the final sulphur content of the steel and attributed this to the intervention of checker reactions.

Harders, Grewe and Oelsen (24) recently carried out sulphur balances on 25 heats in a furnace using mixtures of coke-oven gas, blast furnace gas and producer gas. They found that there was a considerable absorption of sulphur by the slag and metal from the gas phase during charging and melting. Although there was found to be in many cases an increase in the sulphur content of the metal + slag in the refining

period also, the sulphur content of the metal itself was reduced due to sulphur transfer from metal to slag during this period. The decrease in the metal sulphur content during the boil was found to be smaller with increasing sulphur content in the gas. These results clearly show that sulphur can be picked up from the gas phase during the refining period, although they do not indicate whether the sulphur is transferred from the furnace gases to the slag directly or indirectly via molten metal globules thrown up through the slag into the gas phase by the action of the boil.

The qualitative conclusions of such works data were followed by a paper giving theoretical calculations on slag-gas sulphur reactions by Richardson and Withers(25). They represented the slag-gas sulphur reaction thus.

$$\tfrac{1}{2}O_2 + (S^{--}) = \tfrac{1}{2}S_2 + (O^{--})$$

$$K_{slag\text{-}gas} = \frac{(O^{--})\, p^{\frac{1}{2}}_{S_2}}{(S^{--})\, p^{\frac{1}{2}}_{O_2}}$$

Although experimental values for the equilibrium constant for this reaction were not available, Richardson and Withers circumvented this difficulty by using the gas-metal equilibrium.

$$\tfrac{1}{2}O_2 + [S] = \tfrac{1}{2}S_2 + [O]$$

$$K_{gas\text{-}metal} = \frac{p^{\frac{1}{2}}_{S_2}\,[O]}{p^{\frac{1}{2}}_{O_2}\,[S]} \quad \text{or} \quad \frac{p^{\frac{1}{2}}_{S_2}}{p^{\frac{1}{2}}_{O_2}} = K_{gas\text{-}metal}\,\frac{[S]}{[O]}$$

and by defining the slag in terms of the [O] and [S] values with which it would be in equilibrium. Thus values of the ratio $(p^{\frac{1}{2}}_{S_2})/(p^{\frac{1}{2}}_{O_2})$ in equilibrium with any slag defined in this manner could be calculated.

This approach to the problem showed that the metal can lose sulphur to the gas phase via the slag, even though the same metal in direct contact with the gas would pick up sulphur, this sulphur transfer from a lower to a higher sulphur potential being made possible by the simultaneous movement of oxygen from a higher to a lower potential, i.e., from the gas via the slag to the metal. The results of Richardson and Wither's calculations were presented in the form of curves showing the amount of sulphur which the gas phase could contain, at different gas CO/CO_2 levels and temperatures, before transfer of sulphur to the slag occurred. High temperatures and low CO/CO_2 ratios increased the tendency for this transfer to occur.

Such a treatment depends strictly on the condition of non-oxidation of the slag being fulfilled. This condition is not obtained in practice, since, at high oxygen potentials, (O^{--}) is reduced due to Fe_2O_3 formation. Richardson and Withers, however, were able to show that the reduction of (O^{--}) which might be expected was relatively unimportant - as was also (SO_4^{--}) formation, except at very low CO/CO_2 ratios. The work of Richardson and Fincham has shown that the conclusions of the former workers can be taken as substantially correct.

Thus, while the gas phase variables which play an important part in the desulphurisation problem have been dealt with adequately by Richardson and co-workers, the present work is intended to elucidate more clearly the factors involved in desulphurisation from the point of view of the constitution of the slag phase.

CHAPTER III.

THEORETICAL CONSIDERATIONS.

The reaction by which a lime-bearing slag absorbs sulphur from a gas containing SO_2, CO and CO_2 may be represented chemically by the equations:-

$$CaO + SO_2 + 3CO = CaS + 3CO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

and $$CaO + SO_2 + CO_2 = CaSO_4 + CO \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Fincham and Richardson(15) have shown that when p_{O_2} is less than about 10^{-5} atmospheres, a sulphur atom can enter the slag only by displacing a suitable oxygen atom and the sulphur is then held in the slag entirely as sulphide, corresponding to reaction (1) above. When p_{O_2} is greater than about 10^{-3} atmospheres, the sulphur is held entirely as sulphate, corresponding to reaction (2) above. These workers have also shown that, in $CaO-Al_2O_3-SiO_2$ slags, CaO is the only effective oxide in the absorption of sulphur and that no significant proportion of the sulphur is linked to silicon or aluminium, as, for example, in SiS_2 or Al_2S_3.

In the present investigation into the absorption of sulphur from $CO-CO_2-SO_2$ gases by $CaO-Al_2O_3-SiO_2$ slags, the p_{O_2} of the gases used varied within the range 2×10^{-9} to 2×10^{-8} atmospheres (see Appendix). Therefore, the only reaction which need be considered is that represented by equation (1) above. For the purposes of a thermodynamic computation of the activity of CaO, it is more convenient to express it in the form

$$(CaO) + \tfrac{1}{2}S_2 = (CaS) + \tfrac{1}{2}O_2 \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

where round brackets denote concentrations in the slag phase. The equilibrium constant is then represented by

$$K = \frac{a_{CaS}}{a_{CaO}} \cdot \frac{(p_{O_2})^{\frac{1}{2}}}{(p_{S_2})^{\frac{1}{2}}}$$

$$\therefore a_{CaO} \propto a_{CaS} \frac{(p_{O_2})^{\frac{1}{2}}}{(p_{S_2})^{\frac{1}{2}}}$$

The most satisfactory method of obtaining a value for the ^{a}CaO of a slag is to refer unit activity to a slag in equilibrium with solid CaO. Therefore, if a_{CaO} and a_{CaS} refer to the activities of CaO and CaS in a slag in equilibrium with a gas of oxygen and sulphur potentials p_{O_2} and p_{S_2} respectively, and if a slag of unit CaO activity, in equilibrium with a gas of oxygen and sulphur potential $p^{\circ}_{O_2}$ and $p^{\circ}_{S_2}$ respectively has a CaS activity of a°_{CaS}, then the value of the activity of CaO of the first slag is given by

$$a_{CaO} = \frac{a_{CaS} \cdot (P_{O_2})^{\frac{1}{2}} \cdot (p^{\circ}_{S_2})^{\frac{1}{2}}}{a^{\circ}_{CaS} \cdot (p^{\circ}_{O_2})^{\frac{1}{2}} \cdot (p_{S_2})^{\frac{1}{2}}}$$

Hence the determination of a_{CaO} of a slag depends on a knowledge of a_{CaS} of the slag when it is in equilibrium with a gas of known p_{O_2} and p_{S_2}, and of a_{CaS} of the standard slag when it is in equilibrium with a gas of known p_{O_2} and p_{S_2}.

If the ratio $(p_{S_2})^{\frac{1}{2}}/(p_{O_2})^{\frac{1}{2}}$ of a gas is denoted by A, then

$$a_{CaO} = \frac{a_{CaS} \cdot A^{\circ}}{a^{\circ}_{CaS} \cdot A}$$

And A may be termed the "sulphurising potential" of the gas. This chapter is therefore concerned with

(a) the choice of a standard slag,

(b) the determination of a_{CaS} of a slag, and

(c) the determination of the A value of a gas.

(a) The choice of a standard slag.

The thermal equilibrium diagrams of the systems $CaO-Al_2O_3$, $CaO-SiO_2$ and $CaO-Al_2O_3-SiO_2$ are shown in Figs. 1, 2 and 3, respectively, the former being taken from Eitel(26) and the latter two from Hall and Insley's collection (27). In the $CaO-Al_2O_3$ system, it can be seen that, at the experimental temperature of 1500°C, the liquid range extends from 42 - 56·5% CaO. At 1500°C, no melt is in equilibrium with solid CaO, although, by extrapolation of the CaO liquidus below 1535°C, the 1500°C isotherm cuts it at approximately 59% CaO and, as will be shown in the results, the value of a_{CaO} in $CaO-Al_2O_3$ slags when extrapolated to 59% CaO agrees well with that of the standard slag.

In the $CaO-SiO_2$ system there are two ranges liquid at 1500°C - 35-42·5% and 52-56% CaO. Again no liquid is in equilibrium with solid CaO.

In the $CaO-Al_2O_3-SiO_2$ system, there is a considerable range liquid at 1500°C, as indicated by the two areas within the 1500°C isothermal in Fig.3. It will be observed that along a small part of this isothermal, marked MN liquid slags are in equilibrium with solid CaO. Accordingly one slag on this line, composed of 60·5% CaO, 7·0% SiO_2 and 32·5% Al_2O_3 (slag AS1) was chosen as the standard slag, of unit lime activity.

(b) The determination of $^{a}C_aS$ of a slag.

The activity of CaS in a slag cannot be determined from the present study. However, the sulphide content of each slag can be

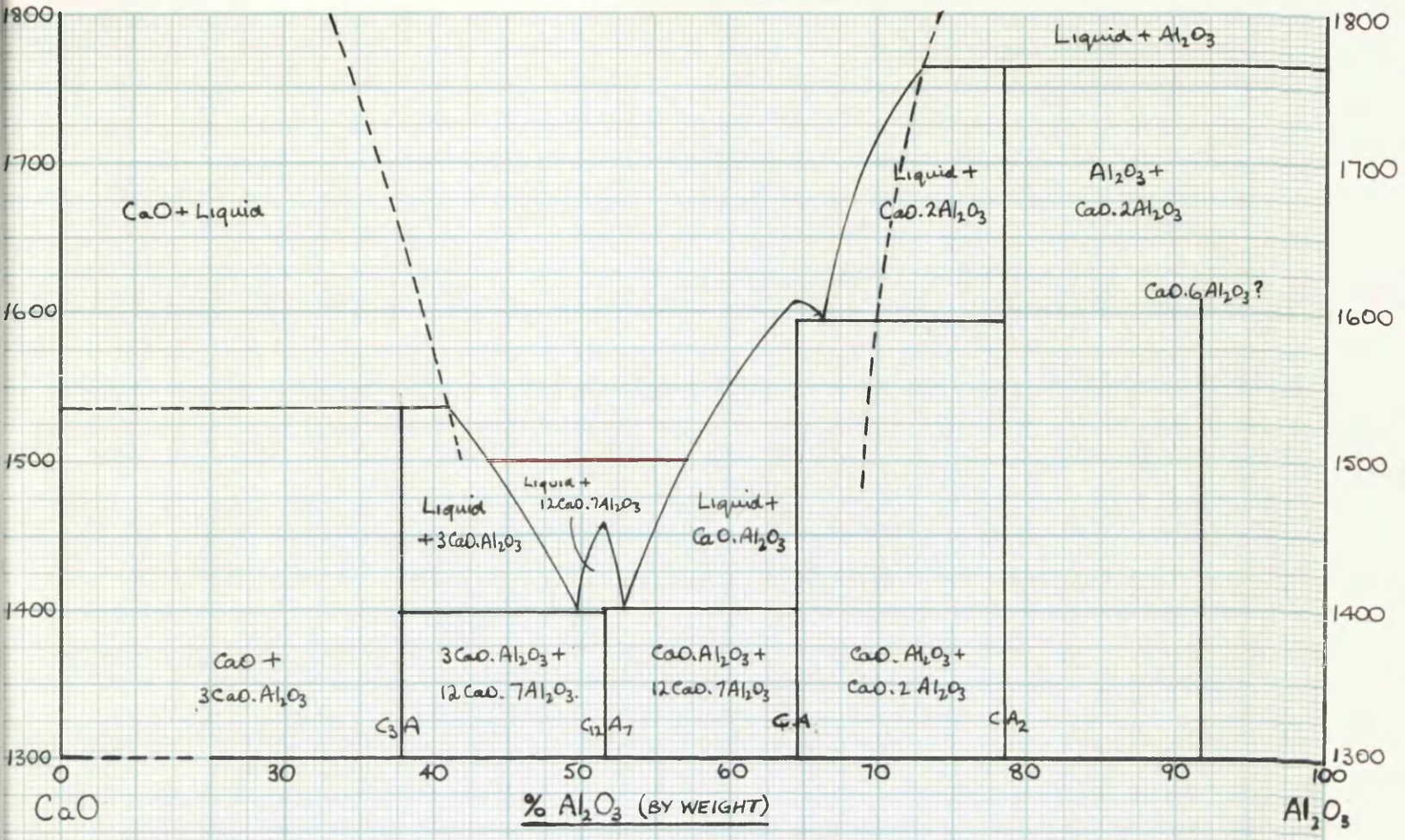


FIG. 1 : CaO-Al_2O_3 PHASE DIAGRAM.

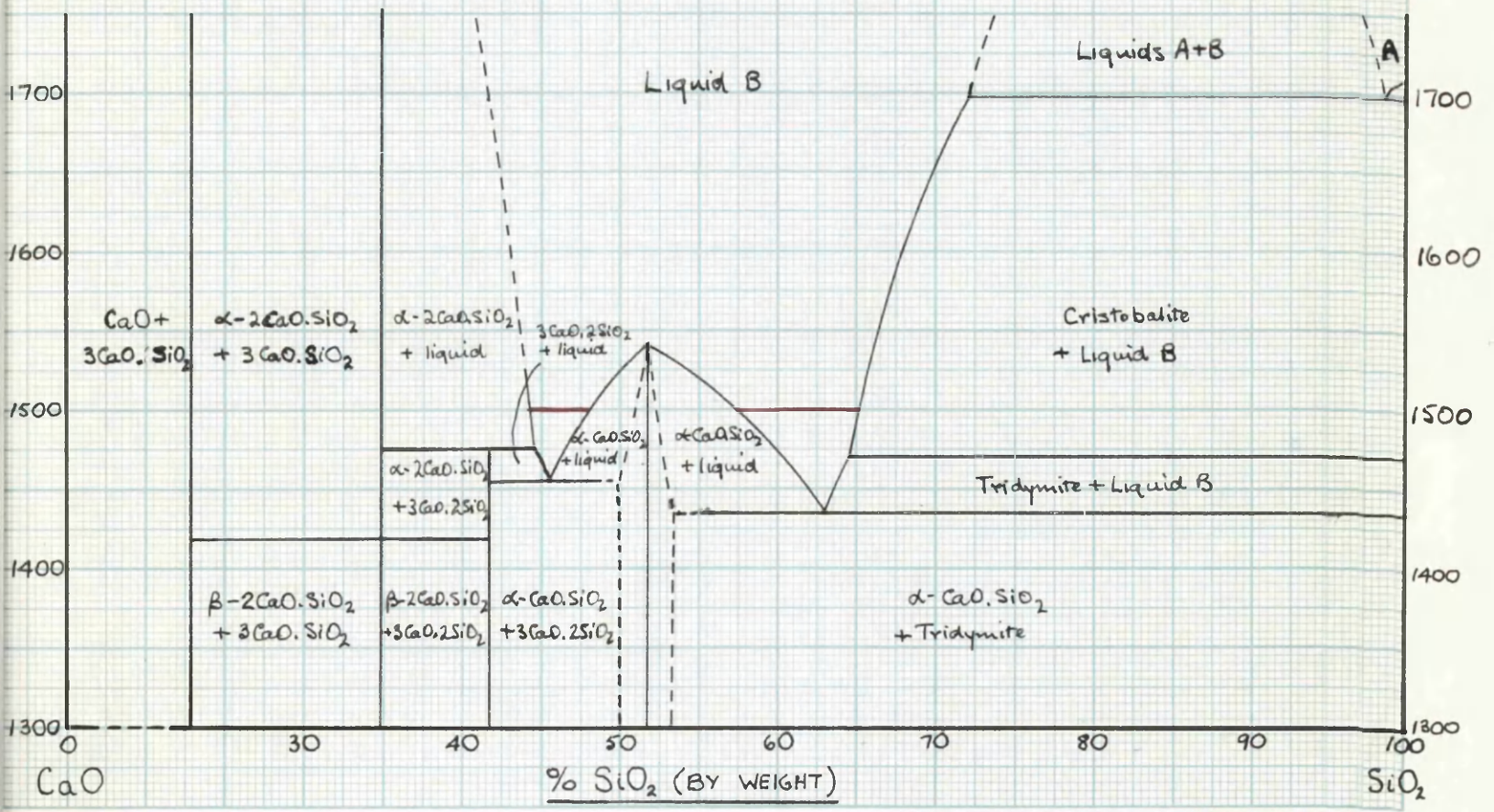


FIG. 2 : CaO-SiO_2 PHASE DIAGRAM.

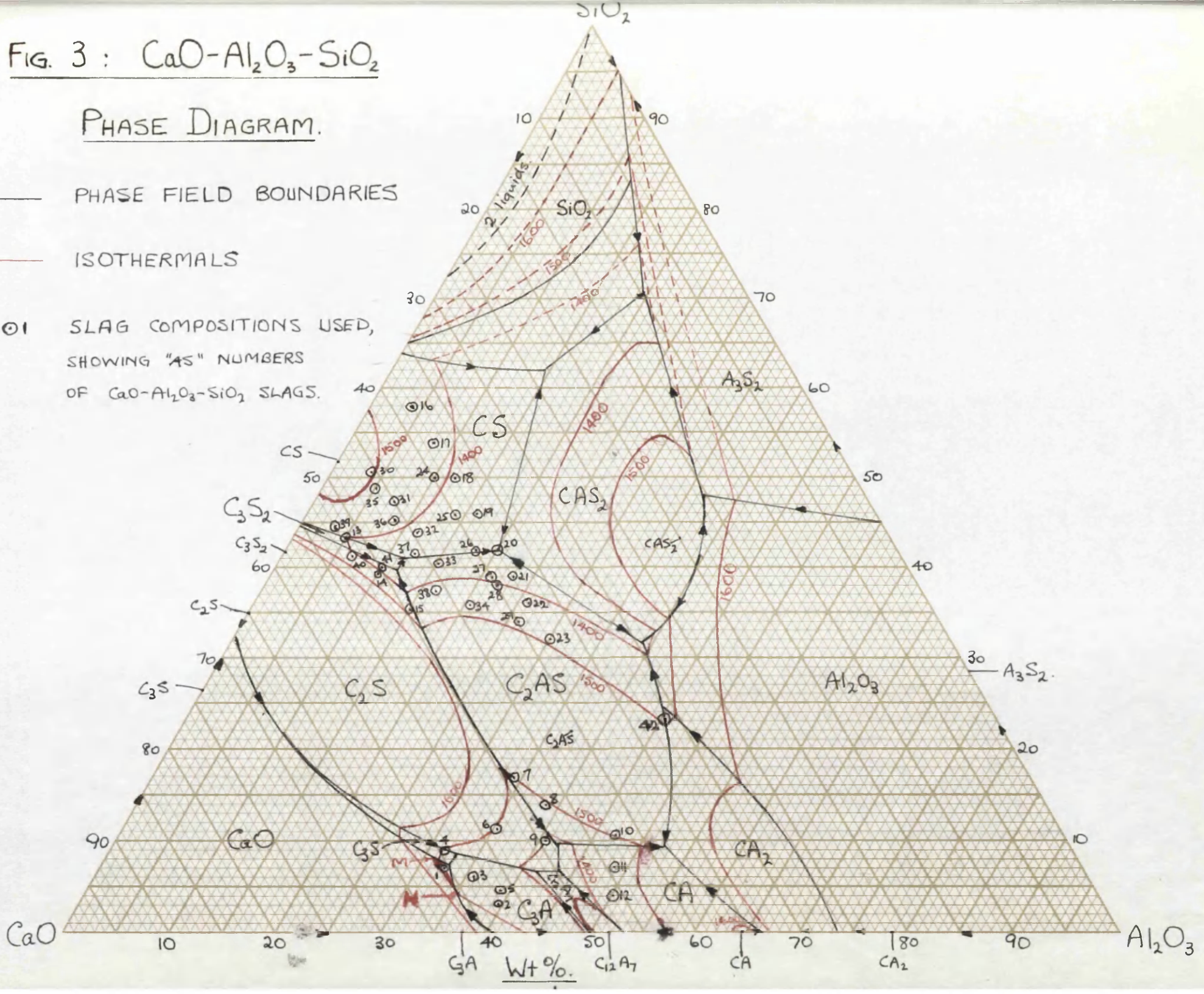
FIG. 3 : $CaO-Al_2O_3-SiO_2$

PHASE DIAGRAM.

——— PHASE FIELD BOUNDARIES

——— ISOTHERMALS

⊙1 SLAG COMPOSITIONS USED, SHOWING "AS" NUMBERS OF $CaO-Al_2O_3-SiO_2$ SLAGS.



obtained by analysis. To use the sulphide data, it is therefore necessary to make certain assumptions, viz:

(1) that the activity of CaS in a given slag is proportional to the %S in the slag,

(2) that the activity of CaS does not vary with the slag composition.

In order to estimate the a_{CaO} value of a slag by this method it is also necessary to assume

(3) that the activity of CaO in the liquid slag is not significantly lowered by the substitution of small amounts of sulphide for oxide.

These assumptions will only hold below a certain limiting value of sulphur content in the slag, and such a limit must be set as a guide to the composition of the gas with which the slags are to be equilibrated in each experiment.

Obviously this limiting value must be below the sulphur saturation value of the slag. Various workers have given values for this: Glaser(28) found the solubility of sulphur in liquid $CaSiO_2$ to be 5% at 1500°C; Filer and Darken(29) found the sulphur saturation limit in blast furnace slags to be 3·5 - 4·5% S at 1500°C; MacCaffery and Oesterle(30) found the solubility of CaS in $CaO-Al_2O_3-SiO_2$ melts at 1500°C to correspond to about 8% S for acid melts and 11% S for more basic melts; Martin, Glockler and Wood(31) studied the forms of sulphur in blast furnace slags and record that the solubility of CaS in a $CaO-Al_2O_3-SiO_2$ slag is 3·6% CaS at 1400-1425°C, i.e., 1·6% S. Fincham and Richardson(15) attributed certain abnormally high results to saturation with CaS. The example given by them is 4·2% S in a 41%

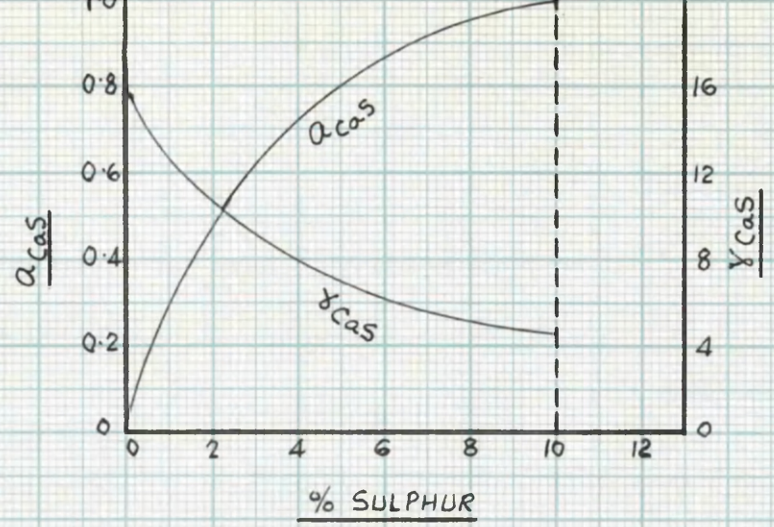


FIG. 4: ACTIVITY OF CaS IN BLAST FURNACE SLAGS [ROSENQVIST (32)].

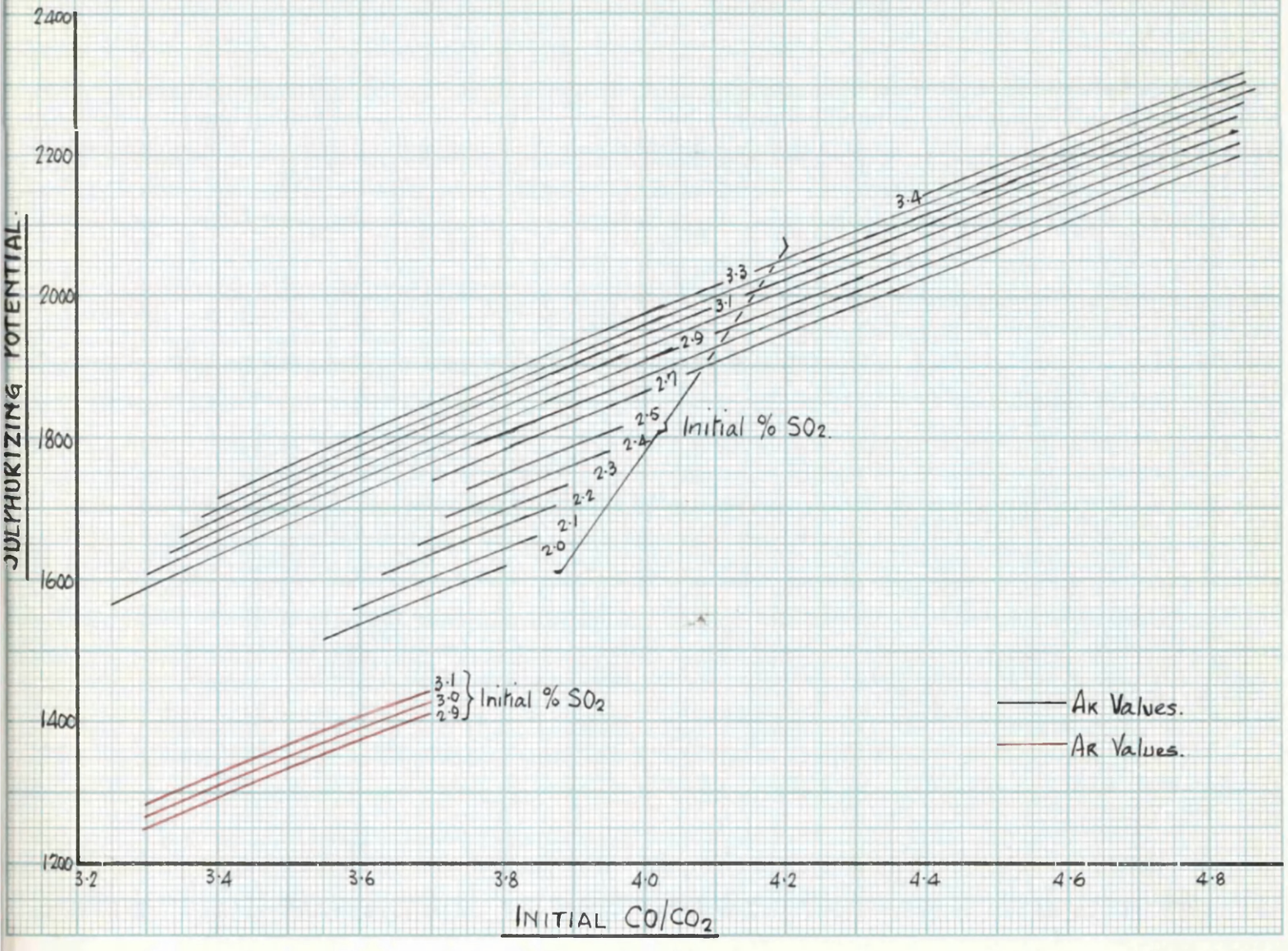


FIG. 5: SULPHURIZING POTENTIALS OF $CO-CO_2-SO_2$ GASES. (1500°C.)

CaO - 52% Al_2O_3 - 7% SiO_2 slag at 1500°C., and from their results it can be calculated, as shown in the Appendix, p.110, that the expected sulphur content of this slag is approximately 1·9%S, which indicates that the sulphur saturation limit for this slag is less than 1·9%S at 1500°C. In the present work two preliminary results (see Table VI, p.59, run 88) of 4·5 and 6·1%S were obtained in a run using a CaO-Al_2O_3 slag containing 54·4% CaO, the resultant slags have a peculiar bulbous appearance. Subsequent work showed that the expected sulphur content should have been about 2·9% S. These results are therefore to be attributed to saturation with CaS, indicating that the sulphur saturation limit for this slag is less than 2·9% S. However, these sulphur saturation values would be expected to be considerably higher than the limiting sulphide concentration which is in keeping with assumptions (1) and (3) above.

Rosenqvist(32) applied his results to those of Hatch and Chipman(33) to derive the graph shown in Fig.4 for the activity of CaS in synthetic blast furnace slags (CaO-SiO_2-MgO-Al_2O_3 slags containing 5-26% Al_2O_3 and 0·1-19% MgO.) However, in deriving this graph, Rosenqvist makes several assumptions whose validity he does not justify, viz.

(1) He assumes that sulphide saturation occurs at 10% S - which figure is rather higher than most of the data quoted above. In addition, the data of Hatch and Chipman, which he uses for the derivation of this graph and for the estimation of the sulphur saturation value, are probably not accurate enough for this purpose.

(2) He assumes that the activity of CaO in a complex CaO-MgO-Al_2O_3-SiO_2 slag of a given $\frac{CaO + \frac{2}{3}MgO}{SiO_2+Al_2O_3}$ ratio is the same as that in a simple CaO-SiO_2 slag of the same CaO/SiO_2 ratio.

(3) He assumes that the absorption by a slag of sulphur contents of up to 5% does not result in any change in its a_{CaO} value.

On account of these criticisms no great stress can be laid on Rosenqvist's graph. The form of the graph of a_{CaS} v. %S should, however, be similar to that shown by Rosenqvist.

Fincham and Richardson(15) have shown that for a given CaO-Al_2O_3-SiO_2 slag at 1500°C, the function $(\%S)(p_{O_2})^{\frac{1}{2}}/(p_{S_2})^{\frac{1}{2}}$ was constant over a range of sulphur contents from 0·003% to approximately 1·3%. Since constancy must be shown by the function $a_{CaS}\cdot(p_{O_2})^{\frac{1}{2}}/(p_{S_2})^{\frac{1}{2}}$, a_{CaS} is therefore proportional to % S, i.e., γ_{CaS} is constant, over this range of sulphur contents. The limit to which this constancy of γ_{CaS} extends in the CaO-Al_2O_3-SiO_2 slags used in the present work is not known. However, a value of 2% was decided upon as the limit below which a_{CaS} could be taken as proportional to the sulphur content of the slag, and below which a_{CaO} would not be significantly affected by the substitution of small amounts of sulphide for oxide in the melt. If this limiting value is too high, then errors will be introduced into the values of a_{CaO} obtained, and the direction of these errors can be shown as follows. Fig.4 shows that as %S increases, γ_{CaS} decreases. Therefore, if the value of a_{CaS} is taken to be correct at say 2% S, the value of a_{CaS}

at 0·05% S will be higher than would have been the case if γ_{CaS} had been constant over the range 0-2% S. Hence if the standard slag of $a_{CaO} = 1$, and a slag of low a_{CaO} are both brought to equilibrium with the same $CO-CO_2-SO_2$ gas giving S° and S% sulphur respectively,

$$a_{CaO} \propto \frac{a_{CaS}}{a^{\circ}_{CaS}} = \frac{\gamma_{CaS}.N_{CaS}}{\gamma_{CaS}.N^{\circ}_{CaS}} = \frac{\gamma_{CaS}}{\gamma^{\circ}_{CaS}} \cdot \frac{S}{S^{\circ}}$$

In calculating the a_{CaO} value of a slag in the present work, the assumption made is that

$$a_{CaO} \propto \frac{S}{S^{\circ}}$$

i.e., that γ_{CaS} is constant over the range 0 - 2% S and for all slag compositions used. The error, therefore, is such as would tend to give a low value to a_{CaO} and would increase as γ_{CaS} increased, i.e., as the sulphur content of the slag decreased. In the present work data will be presented to show that γ_{CaS} in the standard slag is constant up to 1·8% S. However, it is felt that the largest assumption being made in the present investigation is the constancy of γ_{CaS} throughout the considerable range of slag compositions used.

(c) <u>The determination of the sulphurising potential, A, of the gas.</u>

To calculate A, the data required are:-

(1) the free energy change for the reaction

$$2CO + O_2 = 2CO_2$$

Richardson and Jeffes(34) give

$$\Delta G^{\circ}_T = -135,100 + 41·5T \text{ cals.}$$

$$\text{hence } \Delta G^{\circ}_{1773} = -61,520 \text{ cals.}$$

$$\text{and } K_{1773} = 3·84 \times 10^7$$

(2) the free energy changes for the formation of the gaseous compounds of sulphur, carbon and oxygen from SO_2 and CO. This data was initially obtained from Kelley(35). Later, however, the data collected by Richardson and Jeffes(36) became available. The value of A obtained using the data of Kelley is therefore denoted by A_K, and that using the data of Richardson and Jeffes by A_R.

The following are the equations for ΔG°_T derived from Kelley's data, with the values of ΔG°_{1773} and K_{1773}.

TABLE 1.

Reaction	ΔG°_T (cals.)	ΔG°_{1773} (cals.)	K_{1773}
$S_2+2O_2=2SO_2$	$-172,630+3\cdot43T\log T - 0\cdot712\times10^{-3}T^2 + 0\cdot168\times10^5T^{-1} + 24\cdot30T$	-112,020	$6\cdot46\times10^{13}$
$SO_2=S+O_2$	$+137,620-4\cdot56T\log T + 0\cdot578\times10^{-3}T^2 - 0\cdot084\times10^5T^{-1} - 16\cdot9T$	+83,200	$5\cdot31\times10^{-11}$
$SO_2=SO+\frac{1}{2}O_2$	$+79,760-1\cdot715T\log T + 0\cdot356\times10^{-3}T^2 - 0.084\times10^5T^{-1} - 13\cdot5T$	+47,060	$1\cdot58\times10^{-6}$
$SO_2+CO=COS+O_2$	$+62,390-6\cdot80T\log T + 1\cdot536\times10^{-3}T^2 + 0\cdot662\times10^{-5}T^{-1} + 21\cdot45T$	+66,070	$7\cdot16\times10^{-9}$

The data for S_6, S_8 and SO_3 showed that, within the range of gas compositions being used the amounts formed of these compounds would be negligible, while calculations using the data for CS_2 showed that the partial pressure of CS_2 would never exceed 0·1% of the total partial pressure of all sulphur-bearing gases in the gas mixture, and therefore it also was neglected.

The data of Richardson and Jeffes(36) gave the following equations for ΔG°_{T} and the derived values of ΔG°_{1773} and K_{1773} as follows.

TABLE II.

Reaction	ΔG°_{T} (cals)	Estimated Accuracy	ΔG°_{1773} (cals)	K_{1773}
$S_2+2O_2=2SO_2$	-173,240+34.62T	±1 Kcal.	-111,850	$6\cdot03\times10^{13}$
$SO_2=S+O_2$	+125,250-32.16T	±5 Kcals.	+ 68,220	$3\cdot89\times10^{-9}$
$SO_2=SO+\frac{1}{2}O_2$	+ 62,120-18.56T	± >5 Kcals.	+ 29,210	$2\cdot51\times10^{-4}$
$SO_2+CO=COS+O_2$	+ 63,760+1·39T	±2 Kcals.	+ 66,220	6.86×10^{-9}

Data are also given for carbon monosulphide, CS, but it can be shown that, within the range of gas compositions being used, the amount of CS formed is negligible.

Before making any comparison between the two sets of data and their reliability, a sample calculation, by which the A_K value of a gas was obtained, will be shown.

Given the initial CO/CO_2 and $\%SO_2$ of a gas, the mathematics involved in calculating its A_K value are very complex. Consequently a simpler way is to assume figures for the equilibrium CO/CO_2 and the total partial pressure of all sulphur-bearing compounds in the equilibrium gas and by calculation, the values of p_{O_2} and p_{S_2}, and therefore A_K in the equilibrium gas, and also the initial CO/CO_2 and $\%\ SO_2$ can be obtained.

By carrying out a sufficient number of such calculations graphs can be drawn of A_K v. initial CO/CO_2 at various initial CO/CO_2 levels. An example of the calculation will make this clear.

Consider a gas at 1500°C, 760 mm. pressure with an equilibrium CO/CO_2 of 1·46 and the equilibrium total partial pressure of all sulphur-containing compounds = 0·0062 (denote this by Σp_S).

Then $p_{O_2} = 1{\cdot}218 \times 10^{-8}$, $p_{CO} = 0{\cdot}5899$, $p_{CO_2} = 0{\cdot}4039$

and $\Sigma p_S = p_{SO_2} + p_S + p_{S_2} + p_{SO} + p_{COS} = 0{\cdot}0062$

From the K_{1773} values for the various reactions producing these S compounds we have:-

$$p_S = \frac{5{\cdot}309 \times 10^{-11}}{1{\cdot}218 \times 10^{-8}} \cdot a = 0{\cdot}00436a$$

$$p_{S_2} = \frac{1}{6{\cdot}461 \times 10^{13} \times 1{\cdot}218^2 \times 10^{-16}} \cdot a^2 = 104{\cdot}2a^2$$

$$p_{SO} = \frac{1{\cdot}578 \times 10^{-6}}{1{\cdot}218^{\frac{1}{2}} \times 10^{-4}} \cdot a = 0{\cdot}0143a$$

$$p_{COS} = \frac{7{\cdot}162 \times 10^{-9}}{1{\cdot}218 \times 10^{-8}} p_{CO} \cdot a = 0{\cdot}3466a$$

$\therefore$ $104{\cdot}2a^2 + a(1 + 0{\cdot}0044 + 0{\cdot}0143 + 0{\cdot}3466) = 0{\cdot}0062$

which gives the equilibrium percentages of the sulphur-containing compounds as follows:-

$SO_2 = 0.3572\%$, $S = 0.0016\%$, $S_2 = 0.1330\%$,

$SO = 0.0051\%$, $COS = 0.1238\%$, and $A_K = 331$.

To determine the composition of the initial CO-CO_2-SO_2 gas, it can be shown, by considering the changes in gas volumes in a series of reactions of SO_2 with CO giving CO_2 and each of the sulphur-containing compounds already considered,

e.g., $SO_2 + 2CO = 2CO_2 + S$

that

the initial volume of $SO_2 = p_{SO_2} + p_{S_2}$,

the initial volume of $CO = p_{CO} + 2p_S + 4p_{S_2} + p_{SO} + 3p_{COS}$,

and the initial volume of $CO_2 = p_{CO_2} - 2p_S - 4p_{S_2} - p_{SO} - 2p_{COS}$

In the present example, the data give:

initial volume of $SO_2 = 0.00753$

initial volume of $CO = 0.5990$

initial volume of $CO_2 = 0.3961$

Total $= 1.0026$

$\therefore$ initial % $SO_2 = 0.752\%$ and initial $CO/CO_2 = 1.512$

A series of similar calculations gave the following results:

Σp_S	Initial Gas Composition CO/CO_2	$\%SO_2$	A_K
0.0062	1.512	0.752	331
0.0066	1.517	0.805	347
0.0070	1.522	0.859	364
0.0074	1.527	0.914	381

From a graph of these results the following data were obtained:

Initial Gas Composition		A_K
$\%SO_2$	CO/CO_2	
0.77	1.514	336
0.80	1.517	346
0.83	1.519	355
0.86	1.522	364
0.89	1.525	373
0.92	1.527	383

From similar calculations and graphs, based on equilibrium CO/CO_2 values of 1.42, 1.50 and 1.54, similar values were obtained, and these results were then graphed as shown in Fig.6. This graph was then used to determine the A_K values of a gas with an initial CO/CO_2 within the range 1.45 - 1.65 and an initial $\%SO_2$ within the range 0.77 - 0.92 by interpolation between the curves of varying $\%SO_2$ levels. The data for this graph are contained in the Appendix, calculations numbers 1-24.

Fig.8 gives a general picture of the variation in A_K at initial CO/CO_2 ratios of 1.0 - 4.0 and at initial $\%SO_2$ levels of 0.5, 1.0, 1.5 and 2.0%. The data for this graph are contained in the Appendix, calculations numbers 25 - 40.

Fig.5 gives the variation in A_K in gases of initial CO/CO_2 ratios of 3.2 - 4.9 at initial $\%SO_2$ levels of 2.0 - 3.4. The data for this graph are contained in the Appendix, calculations numbers 41-94.

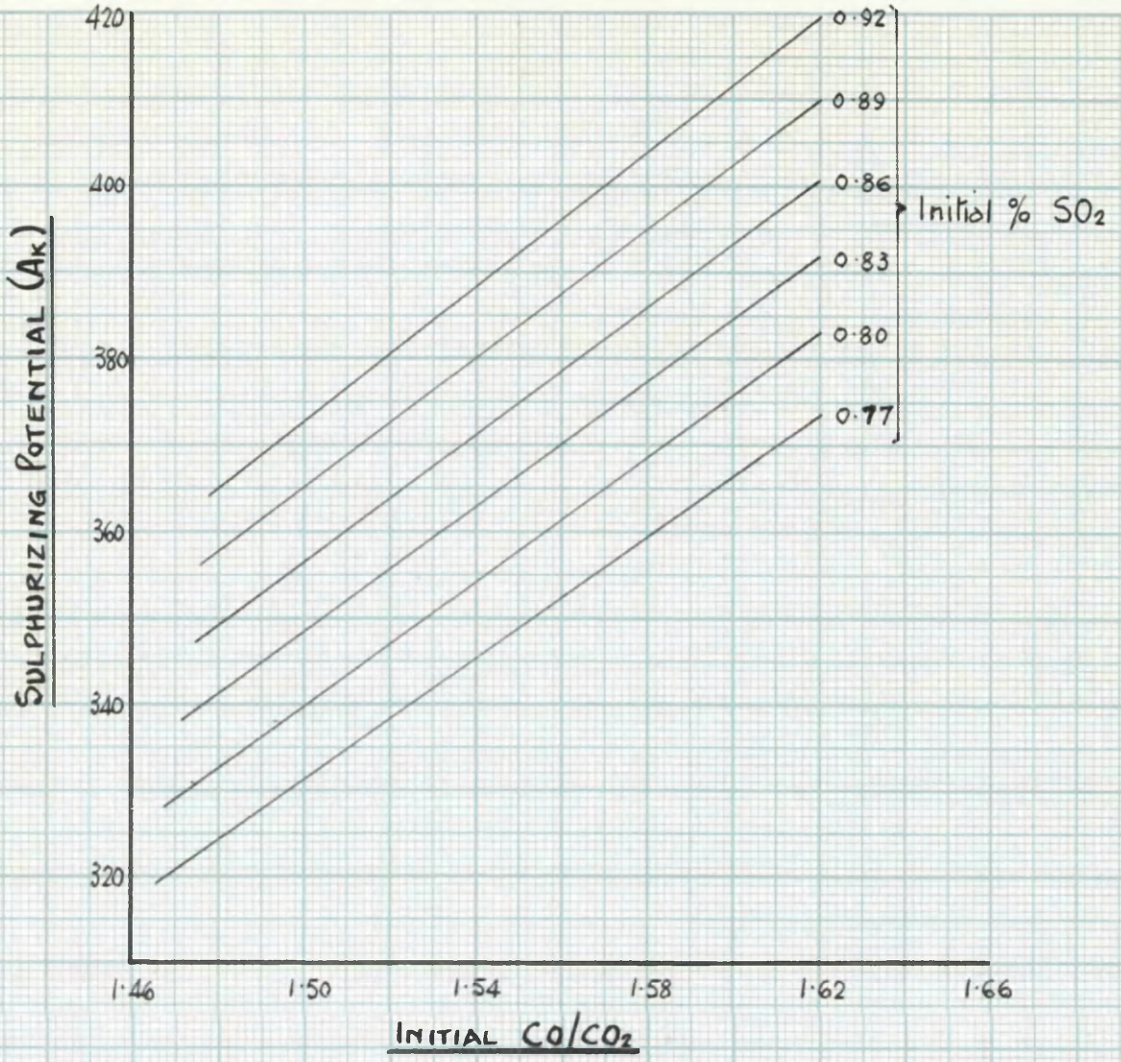


FIG. 6: SULPHURIZING POTENTIAL (A_K) OF $CO-CO_2-SO_2$ GASES AT 1500°C.

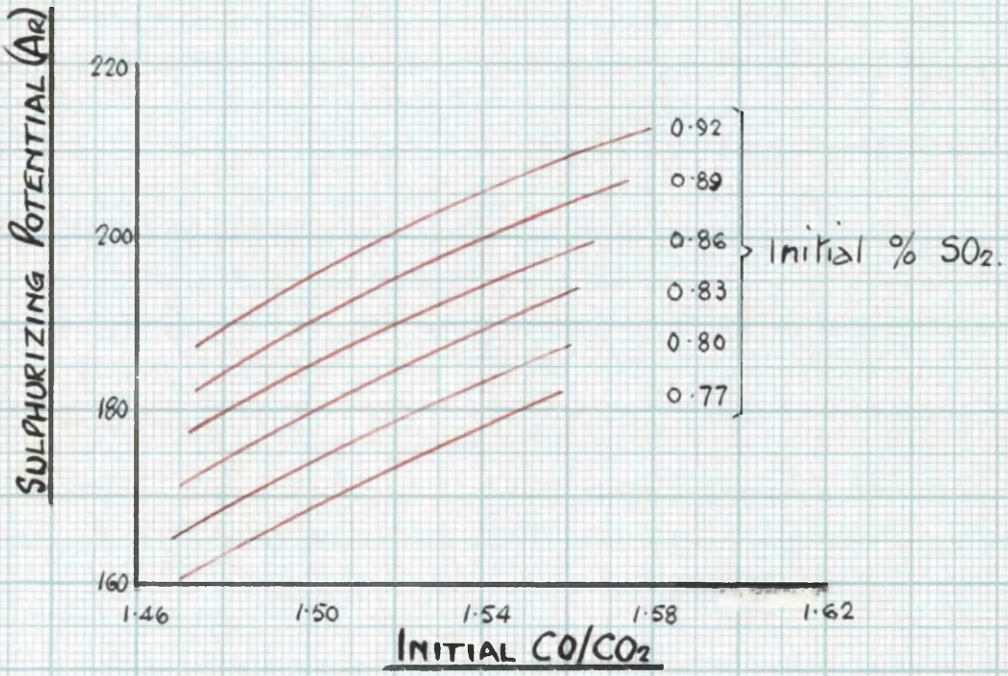


FIG. 7: SULPHURIZING POTENTIAL (A_R) OF $CO-CO_2-SO_2$ GASES AT 1500°C.

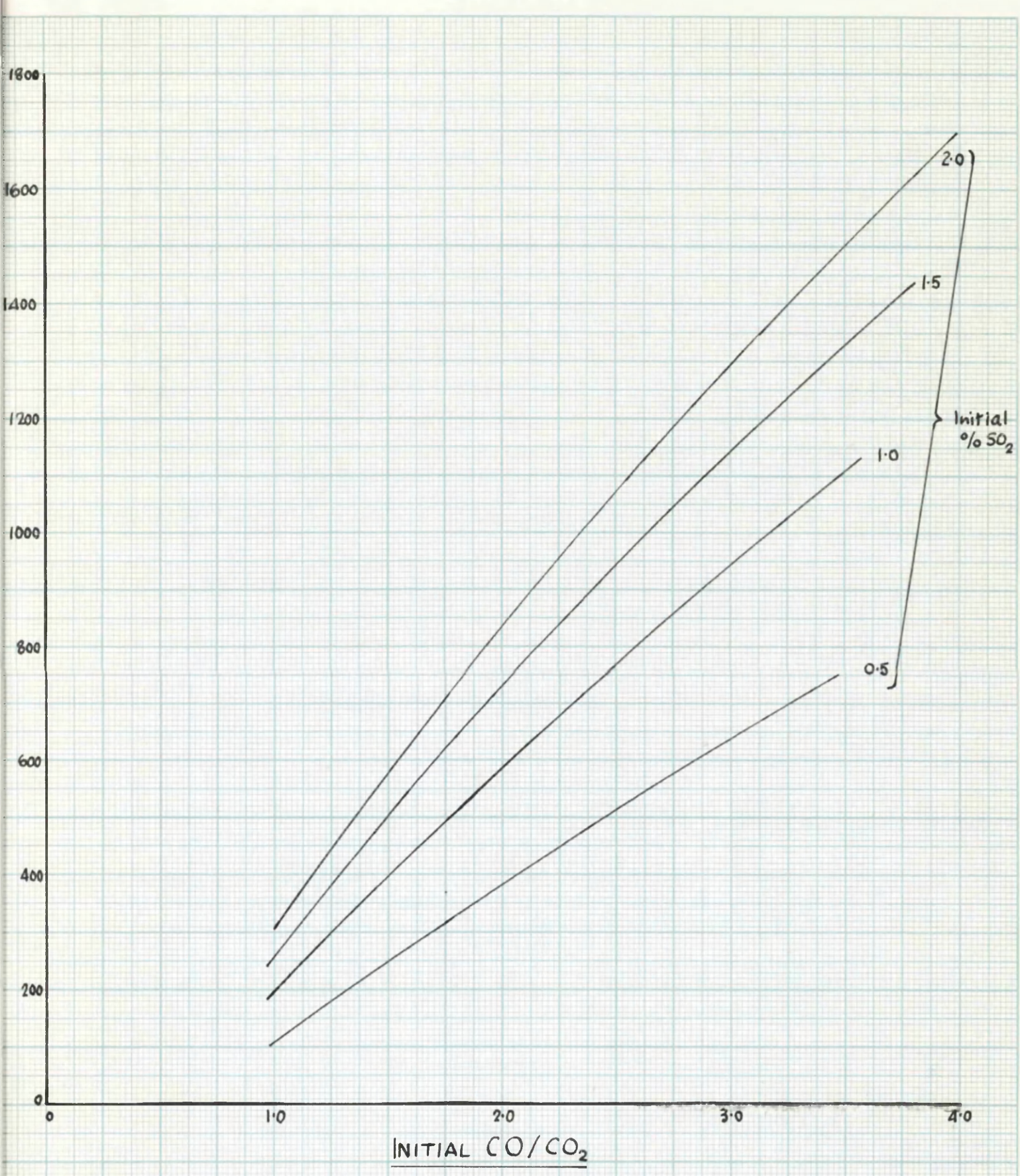


FIG 8 : SULPHURIZING POTENTIALS (A_K) OF $CO-CO_2-SO_2$ GASES AT 1500°C.

Using the data of Richardson and Jeffes(36), values of A_R over ranges of gas composition somewhat similar to those covered by Figs. 5 and 6 were calculated and are shown in Figs.5 and 7, the data used being contained in the Appendix, calculations numbers 101-124.

Comparison of values of A_K and A_R show that there is a considerable difference between the two, particularly at low values of A, e.g.,

(1) for a gas of initial CO/CO_2 of 1.52, initial SO_2 of 0.81% :

$$A_K = 350, \text{ and } A_R = 181;$$

(2) for a gas of initial CO/CO_2 of 3.34, initial SO_2 of 3.01% :

$$A_K = 1640, \text{ and } A_R = 1280.$$

The cause of these differences lies in the discrepancies between the ΔG_T° values of the reactions involving (a) S, and (b) SO.

(a) for $SO_2 = S + O_2$, Kelley gives $\Delta G^\circ_{1773} = 83{,}200$ cals.,
Richardson - 68,200 cals.

(b) for $SO_2 = SO + \frac{1}{2}O_2$, Kelley gives $\Delta G^\circ_{1773} = 47{,}060$ cals.
Richardson - 29,210 cals.

These differences are further seen if the proportions of S and SO to the total sulphur containing gases in an equilibrium gas are compared.

		$\frac{p_S}{\Sigma p_S \text{ compounds.}}$	$\frac{p_{SO}}{\Sigma p_S \text{ compounds.}}$
For gas (1) above	Kelley.	0.0025	0.0083
	Richardson.	0.078	0.55
For gas (2) above	Kelley.	0.0024	0.0045
	Richardson.	0.10	0.39

The sources from which Kelley and Richardson obtained their data were therefore investigated.

For the reaction $SO_2 = S + O_2$ the uncertainty lies in the reaction $S_2(g) = 2S(g)$.

Kelley bases his calculations on corrected spectroscopic data of Montgomery and Kassel(37) giving a dissociation energy ΔH_0° of + 102.6 kcals. This value gives 137.6 kcals. for ΔH_0° of the reaction $SO_2 = S + O_2$.

Richardson and Jeffes(36) quoting Gaydon(38) state that spectroscopic measurements indicate that the dissociation energy of S_2 is most probably 101 $\pm$ 3 kcals., although +83 and +76 are also possible values. Gaydon states that it is impossible to decide between the three values, but indicates a preference for the highest value. Richardson and Jeffes, however, taking into account molecular weight determinations by Nernst(39) and von Wartenberg(40), recommend a value of +73 kcals. for ΔH_0° of $S_2 = 2S$ - which gives +125.2 kcals. for ΔH_0° of the reaction $SO_2 = S + O_2$.

For the reaction $SO_2 = SO + \frac{1}{2}O_2$, the uncertainty lies in the reaction $S + O = SO$.

Kelley bases his calculations on corrected specroscopic data of Montgomery and Kassel(37) giving a ΔH_0° value of -13.1 kcals. for the reaction $S_2 + O_2 = 2SO$. When allowance is made for the dissociation energies of S_2 (+102.6 kcals.) and of O_2 (+118.0 kcals.) this value corresponds to a dissociation energy of SO into its atoms, of +117 kcals., and to +79.8 kcals. for ΔH_0° of $SO_2 = SO + \frac{1}{2}O_2$.

Richardson and Jeffes quote Gaydon(38) as giving two values for the dissociation energy of SO into its atoms, viz., +119.5 kcals. and +92.3 kcals. Although he admits there is no conclusive evidence on the point, Gaydon prefers the higher value, and Richardson and Jeffes accept this value. When this value is combined with Richardson and Jeffes'

most probable value for the dissociation energy of S_2 (+ 73 kcals.,) and with the dissociation energy of O_2 (+117.2 kcals.,) it gives - 49 kcals. for ΔH°_3 of the reaction $S_2 + O_2 = 2SO$, and 62.1 kcals. for ΔH°_0 of $SO_2 = SO + \frac{1}{2}O_2$. Richardson and Jeffes also note that if the lower value for the dissociation energy of SO (+92.3 kcals.) is used, ΔH°_0 of the reaction $S_2 + O_2 = 2SO$ becomes +6 kcals. - and accordingly give the corresponding free energy equation the highest error limits.

Since Richardson and Jeffes' collection of data was published, St. Pierre and Chipman(41) have carried out experiments on lime-iron oxide slags, bringing them to equilibrium with SO_2 + CO mixtures at 1550°C. They show that their data lead to a decision between the possible values of the dissociation energies of SO and S_2 quoted by Gaydon, and that they are in favour of values of +119.5 kcals. for ΔH°_3 of $SO = S + O$, and + 83 kcals. for ΔH°_0 of $S_2 = 2S$.

The effect of these discrepancies on the present work may be seen more clearly if several combinations of the possible ΔH°_3 values of $SO = S + O$ and of $S_2 = 2S$ are used in the calculation of the A values of the gases marked (1) and (2) above, and the ratios A_2/A_1 thus obtained, compared as shown in Table III below.

TABLE III.

ΔH°_{298} (kcals./mole)			ΔG°_{1773} (kcals/mole).		Values accepted by	A_2/A_1
SO=S+O	S_2=2S	O_2+S_2=2SO	SO_2=SO+$\frac{1}{2}O_2$	SO_2=S+O_2		
+92.3	+73	+6	+56.6	+68.2		$\frac{1630}{316}$=5.16
+92.3	+83					
+92.3	+101					
+119.5	+73	-49	+29.2	+68.2	Richardson and Jeffes.	$\frac{1280}{181}$ =7.07
+119.5	+83				St.Pierre and Chipman.	not calculated but approx. 6.4.
+117	+102.6	-13.1	+47.1	+83.2	Kelley	$\frac{1640}{350}$ = 4.69

In this Table, A_2/A_1 in the first line is obtained from the data given in the Appendix, calculations 125-6. This line corresponds to the alternative value for the dissociation energy of SO of 92.3 kcals., which Richardson and Jeffes(36) mention but do not favour. Indeed this value is favoured by none of the workers quoted above. Therefore, no values have been calculated for the ratio A_2/A_1 in the second and third lines of the above table. The value of A_2/A_1 shown in the fifth line was obtained by interpolation between the values given in the fourth and sixth lines, since, as the present work will show, it was not necessary to obtain an exact value for this line.

The above table indicates a method by which it should be possible to select the correct data relating to SO and S formation. By bringing samples of the same slag to equilibrium with gases of widely different

A values (e.g., gases (1) and (2) above), an experimental value of the ratio $A_2/A_1 = S_2/S_1$ will be obtained where S_2 and S_1 are the sulphur contents of the slag at equilibrium with gases (1) and (2) respectively.

The Effect of Temperature on A_K.

From the data in the Appendix, calculations numbers 127-130, it can be shown that, for a gas of initial $CO/CO_2 = 1.52$ and initial SO_2 of 0.85%, the rate of change of A_K is -1.30% per °C over the range 1490-1500°C, and -1.28% per °C over the range 1500-1510°C. Therefore at 1500°C, the rate of change is -1.3% per °C.

As most of the experimental work was carried out at 1500°C., the temperature effect on A does not enter into the calculations. The following formula can therefore be used to calculate a_{CaS} :-

$$a_{CaO} = \frac{S/A}{S^\circ/A^\circ}$$

In using this formula the assumptions discussed above must be made. It may be noted in passing that S/A corresponds to the function used by Fincham and Richardson(15) in their work on sulphur in silicate and aluminate slags, viz., the sulphide capacity $C_S = (\%S)(p_{O_2})^{\frac{1}{2}}/(p_{S_2}^{\frac{1}{2}})$.

CHAPTER IV.

EXPERIMENTAL TECHNIQUE.

The apparatus is shown in Fig.9 and consists of three main sections:

(1) apparatus for the production of a steady flow of the required $CO-CO_2-SO_2$ gas mixture;

(2) apparatus for the analysis of the gas mixture; and

(3) the furnace, containing the reaction chamber.

The details of each of these sections will now be outlined in turn.

Gas Production, Purification, Control of Rate of Flow and Mixing.

Carbon dioxide was obtained from cylinders of commercial liquid carbon dioxide, and dried by passing through anhydrone. Analysis of this gas for oxygen gave a figure of 0.04% - which can be neglected as far as its effect on the CO/CO_2 ratio of the gas mixture at equilibrium at 1500°C is concerned.

Sulphur dioxide was obtained from a syphon of the liquid, and dried by passing through anhydrone.

Carbon monoxide was obtained by passing carbon dioxide, obtained from commercial liquid carbon dioxide, over carbon at a high temperature. The carbon used was the powder obtained in drilling graphite electrodes to make crucibles, and was contained in a Pythagoras tube in a Nichrome - wound furnace maintained at 1100-1150°C. In order to prevent the reaction

$$C + H_2O = CO + H_2$$

taking place, the carbon dioxide was dried over anhydrone prior to reaction with the carbon, and the graphite powder was dried at 110°C,

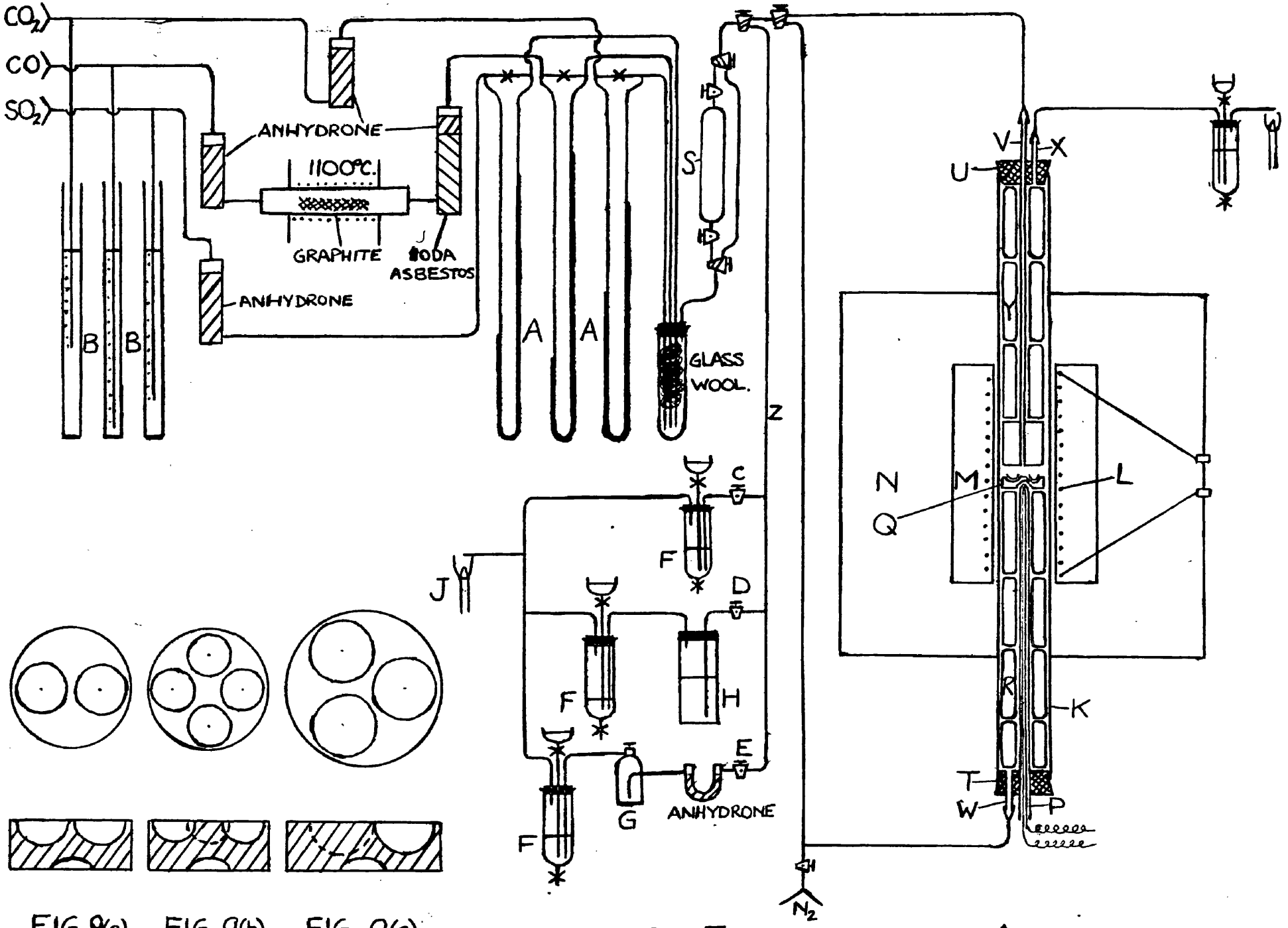


FIG. 9(a) FIG. 9(b) FIG. 9(c)

FIG 9: EXPERIMENTAL APPARATUS

and stored in a desiccator over anhydrone prior to use.

It was at first thought that a CO-CO_2 gas, of the CO/CO_2 ratio desired for the experiments, could be produced directly by control of the Nichrome furnace. However, using the data of Richardson and Jeffes(34) for the reaction

$$CO_2 + C = CO$$

$$\Delta G^{\circ}_T = 40{,}800 - 41.7\ T$$

it can be shown that, at temperatures of

742.5°C 750°C 760°C

the CO/CO_2 ratio obtained at equilibrium is

3.00 3.27 3.79 respectively,

i.e., an increase in temperature of 10°C at 750°C results in an increase of approximately 16% in the CO/CO_2 ratio. The production of a gas of a given CO/CO_2 ratio under these conditions would have required a furnace controlled to a greater degree than was practicable with normal laboratory apparatus. Hence, it was more convenient to produce pure carbon monoxide and obtain the desired CO/CO_2 ratio by mixing with pure carbon dioxide.

Further calculations showed that the % CO_2 remaining in the gas obtained by passing carbon dioxide over carbon at temperatures of

	1000°C	1050°C	1100°C
was	0.8%	0.42%	0.24%

Hence the graphite was maintained at a temperature of not less than 1100°C and the gas obtained was passed through self-indicating soda-asbestos granules to remove the last traces of carbon dioxide.

Another possible source of impurity in the gas would be sulphur in the graphite, but this need cause no anxiety since the reaction products of sulphur would also be removed by the soda-asbestos.

The three gases were each metered by capillary flowmeters, A. The capillaries were constructed by heating short lengths of normal capillary glass tubing in the flame until the constrictions produced were such as to give pressure differences within the range of 20-140 cms. of oil for the ranges of gas flow desired. The indicating liquid used in the flowmeters was Griffin and Tatlock's Special Flowmeter Oil, of very low vapour pressure. The total flow rate of the gas mixture normally used was 140-150 mls. per minute, while in a few runs a flow of 60-70 mls. per minute was used. The gas compositions used varied within the ranges 0.3 - 3.5% SO_2 and 1.0 - 4.8 CO/CO_2 ratio. Hence the flowmeter orifices were such as to give the following ranges of rates of flow:

SO_2	0.5 - 5	mls. per minute;
CO	40 - 120	mls. per minute;
CO_2	25 - 75	mls. per minute.

The flowmeters were calibrated using the same methods as are described later for gas analysis, but because of changes in atmospheric pressure and temperature causing small variations in the flowmeter readings for a given flow of gas (variations of up to $\pm$ 2%) the calibrations were only used as guides and the gas mixture to be used in a run was always analysed immediately prior to the run.

The problem of maintaining a constant flow of each gas was solved by incorporating in each gas system an adjustable bleeder column, B. The depth of water in each column was adjusted so that the desired flowmeter reading was obtained, and the gas cylinder and siphon valves were then closed till a small steady flow of gas was escaping through each bleeder column. By this means adequate control of the gas flow rates was obtained, since the pressure differences across the flowmeters could be kept constant to within $\pm$0.2 cms.

The three gases were then mixed by leading them to the foot of a boiling tube filled with glass wool, the gas mixture being led out at the top of the boiling tube.

Analysis of the Gas Mixture.

On commencing the flow of gases for a run or calibration, the gas mixture was by-passed through the sampling bulb at S and bubbled, via the limb C, through a vessel F with an adjustable water level, to the gas-jet at J where it was burned. After running for at least an hour, the weight of (CO_2 + SO_2) flowing per minute was determined by absorption for a given time in the soda-asbestos midvale bulb, G. The weight of SO_2 flowing per minute was likewise determined by absorption in 100 ml. of 5-volume hydrogen peroxide solution contained in the gas-jar H, the sulphuric acid formed being titrated against N/20 sodium hydroxide solution using methyl yellow as indicator. (Various indicators were tried, but, on account of the carbon dioxide dissolved in the peroxide solution, methyl yellow was found to be the most suitable. The end-point of the titration could be detected, by comparison with a standard colour, to within 0.2 ml., and with practice

this was reduced to within 0.1 ml., the titrations being never less than 10 mls.). Tests showed that, at the maximum rates of gas flow and at the maximum values of % SO_2 used, the depth of solution obtained by using 100 mls. of 5 vol. peroxide solution in a gas jar was sufficient to absorb all the sulphur dioxide in the gas mixture. During these determinations, the depth of water in each of the 3 vessels, F, was adjusted so that the resistance offered to the flow of gas in each of the limbs C, D and E, did not vary, and hence the rates of flow of the gases remained constant during analysis.

When constant duplicate results for the rates of flow of carbon dioxide and sulphur dioxide were obtained, the gas sample in the sampling bulb at S was removed and analysed for the ratio $CO/(CO_2 + SO_2)$. This was done by flushing the sample with CO_2-free nitrogen through an analytical train consisting of a soda-asbestos midvale absorption bulb, followed by a copper oxide tube in a small furnace kept at 400-500°C, and finally a second soda-asbestos absorption bulb. A second copper oxide tube in the furnace followed by a soda-asbestos absorption bulb showed that the conversion of carbon monoxide to dioxide was complete in the first copper oxide tube. The ratio of the gain in weight in the second soda-asbestos absorption bulb to that in the first gave the weight ratio CO_2 (from CO)/ $(CO_2 + SO_2)$. Together with the rates of flow of carbon dioxide and of sulphur dioxide, this data was used to calculate the volumetric CO/CO_2 ratio and the $\%SO_2$ in the gas mixture used in the experimental run.

Another possible source of impurity in the carbon monoxide, in addition to those previously mentioned, was hydrogen adsorbed by the

graphite. As a check on the freedom of the carbon monoxide from hydrogen, an anhydrone U-tube was inserted immediately after the copper oxide tube in the analytical train described above. A sample of carbon monoxide was then passed through the train and it was shown that no measurable quantities of hydrogen were present in the carbon monoxide.

The Furnace and Reaction Chamber.

The runs were carried out using a platinum-wound resistance furnace as shown in Fig.9. The furnace tube, K, was a $1\frac{1}{8}$ in. internal diameter mullite tube, 30 ins. long. (For later experiments a $1\frac{1}{2}$ in. tube was used). This was placed within a thin alundum tube on which was wound the platinum wire, L. This tube was wound over a length of 9 ins. with 20 S.W.G. platinum wire and insulated as shown by fused alumina, M, and diatomaceous brick, N. This furnace gave at 1500°C a hot zone which was constant to within 5°C, over a length of 1.8 ins. The power input to the furnace was controlled by a 16-Amp. Variac autotransformer, by hand adjustment of which the temperature could be maintained at 1500°C $\pm$ 2°C, with only occasional attention.

The temperature was measured by a platinum/13% rhodium-platinum thermocouple housed in a mullite sheath, P, which fitted into a depression in the base of the reaction tray, Q. The thermocouple was regularly standardised against the melting points of gold (1063°C) and palladium (1555°C). The e.m.f. generated by the thermocouple was measured using a Tinsley vernier potentiometer and spot galvanometer. By comparison with another standard couple placed in one of the platinum crucibles in

the reaction tray, a slight correction, never amounting to more than 5°C, was found to be necessary between the reading obtained in the sheath and the actual temperature of the crucibles.

The alundum reaction tray, Q, was supported in the hot zone of the furnace by a series of alundum stools, R, fitting round the mullite sheath, P, and resting on the rubber bung, T, at the base of the furnace tube. The rubber bung, U, at the top of the furnace tube held an alumina tube, V, $\frac{1}{4}$ in., outside diameter, $\frac{1}{8}$ in., internal diameter, through which the gas entered the reaction chamber. The lower bung, T, also held a short gas entry tube, W, and the upper bung, U, a short gas exit tube, X. Another series of alundum stools, Y, fitted over the alumina tube, V, and filled the space between the reaction chamber and the upper bung. The lowest of these stools was cemented onto the alumina gas entry tube, V. The gap between this lowest stool and the top surface of the reaction tray was not more than 0.5 in., and this gap, together with the reaction tray may be conveniently termed the reaction chamber. Thus the reaction chamber was contained entirely within the hot zone of the furnace. The reaction tray itself was 0.4 - 0.5 in., deep and is shown in Figs.9(a), (b) and (c). It contained either (a) two $\frac{3}{8}$ in. diameter, (b) four $\frac{5}{16}$ in. diameter, or (c) three $\frac{7}{16}$ in. diameter, depressions to accommodate the crucibles.

The crucibles were made of platinum since this was the only material which would hold molten slag under the conditions of the experiment. Circles of platinum foil were cold-pressed into a hemispherical shape between a ball-bearing and a wooden block containing a series of

successively deeper depressions. Initially a $\frac{3}{8}$ in. diameter ball-bearing was used and the crucibles obtained were able to hold 0.25 - 0.30 gms. of the powdered slag. Two such crucibles could be accommodated within the $1\frac{1}{8}$ in. reaction tube. Later a $\frac{5}{16}$ in. diameter ball-bearing was used and the crucibles could hold 0.16 - 0.20 gms. of slag. Four such crucibles could be accommodated within the $1\frac{1}{8}$ in. diameter reaction tube. Later still a $\frac{7}{16}$ in. diameter ball-bearing was used and the crucibles could hold 0.40 - 0.45 gms. of slag. Three such crucibles could be accommodated within the $1\frac{1}{2}$ in. reaction tube. These weights of slag were found to be convenient for analysis of sulphur content, and the relatively high ratio of slag surface area to weight of slag facilitated the attainment of equilibrium in a reasonable length of time.

Thus the reaction chamber and reaction tube fulfilled the following requirements.

(a) The possibility of error due to the effects of thermal diffusion, should be, as far as possible, eliminated. When a gas mixture is contained in an unevenly heated system, thermal diffusion results in a higher concentration of the less dense gas in the hotter regions of the system, with a corresponding decrease in the cooler regions. This effect is, of course, greater when using high frequency induction heating, than with a resistance wound furnace. Investigations of the effect have been made by Chapman(42)(43), Ibbs(44)(45), Gillespie(46) and Dastur and Chipman(47) who have shown that the effect increases with increasing ratio of the densities of the component gases, and that it varies with the proportions of the component gases, reaching a maximum when their molar fractions are

equal. Dastur and Chipman also showed that the effect of thermal diffusion in metal-gas equilibria can be minimised by using high flow rates, by preheating the gas mixture to the temperature of the metal, and by dilution of the gas mixture with an inert gas of high molecular weight. The effect of thermal diffusion was not expected to be great in the present experiments, since the ratio of the densities of SO_2, CO_2 and CO is not large, the percentages of SO_2 used were small, and the gases would be preheated to some extent in travelling down the length of the gas inlet tube, V, (Fig.9). Indeed a thermocouple placed within the reaction chamber showed no change in temperature when nitrogen, at the rate of 150 mls. per minute, was passed down the tube, V, through the reaction chamber. The high linear velocity of the gas to and from the reaction chamber, and the fact that the reaction chamber was contained entirely within the hot zone of the furnace, would also tend to prevent thermal diffusion. Later, experiments showed that alteration of the linear velocity of gas flow (by altering the volume rate of gas flow or by using an alumina tube of thinner bore for the gas inlet tube, V) gave results agreeing, within the limits of experimental error, with those obtained using the normal linear velocity of gas flow. Hence it can be concluded that the rate of gas flow and the degree of preheat of the gas mixture are such that the effects of thermal diffusion in the present experiments are within the limits of experimental error.

(b) If required, it should be possible to approach equilibrium from both sides within the same experiment. This was practicable since there were at least two slag samples in each run.

(c) It should permit of a rapid means of freezing the equilibrium. At the end of a run, the lower bung, stools and reaction tray were lowered 2 - 3 ins., immediately after shutting off the gas flow and the power supply. The reaction tray was then removed from the furnace by slowly lowering over a period of 10 minutes. On account of the small bulk of the slag, solidification should be very rapid. Fincham and Richardson(15) have shown that solidification of a similar sample from a rather higher temperature took place in about 10 seconds. In only a very few instances did the reaction tray stick in the tube before it had been lowered sufficiently to cause solidification to take place, and in these instances it was found that the influx of air oxidised some of the sulphide giving low results.

Slag Preparation.

The raw materials used were as follows.

analar calcium carbonate,

analar alumina, and

silica sand.

The silica sand was further purified by boiling with concentrated hydrochloric acid to 99.9% purity.

To cover the range of CaO-Al_2O_3 slag compositions molten at 1500°C, three master slags, containing approximately 42, 48 and 55% CaO respectively, were prepared by calcining weighed quantities of the

calcium carbonate, mixing with the required weights of alumina and fusing in carbon crucibles using high frequency induction heating. The fused slag was then powdered and held in air at 1100°C to reconvert all calcium carbide formed to lime.

To cover the range of $CaO-SiO_2$ slag compositions molten at 1500°C, two slags, containing approximately 35 and 55% CaO respectively, were prepared in a similar fashion to the $CaO-Al_2O_3$ slags.

These five master slags were then analysed. Intermediate compositions in the $CaO-Al_2O_3$ and $CaO-SiO_2$ fields were made by mixing these slags in the necessary proportions. For $CaO-Al_2O_3$ slags of more than 55% CaO, small amounts of analar calcium carbonate were added to the 55% CaO master slag. Ternary $CaO-Al_2O_3-SiO_2$ slags were made by mixing the appropriate quantities of the binary master slags with, if necessary, small quantities of analar calcium carbonate or alumina.

Table IV (p. 54) gives a list of the slag compositions used. For convenience in reference each slag composition has been given a number.

Analysis of Slags.

$CaO-SiO_2$ Slags.

0.4 gm. samples of the slags were fused with fusion mixture and the fusion dissolved in warm water, to which hydrochloric acid was added. Silica was determined by evaporating the solution to dryness and baking; the residue was then boiled with concentrated hydrochloric acid and the silica filtered off. The filtrate was again evaporated to dryness, baked, and the silica filtered off. Silica was then estimated by ignition and volatilisation by hydrofluoric and sulphuric acids.

Lime was estimated in the filtrate from the silica estimation by precipitation as oxalate from faintly alkaline solution, and ignition of the precipitate to CaO.

$CaO-Al_2O_3$ Slags.

0.4 gm. samples of the slags were dissolved by boiling in water and adding concentrated hydrochloric acid dropwise till solution was complete. Lime was estimated by precipitation as oxalate from a slightly alkaline solution buffered by the addition of a 2.5% citric acid - 0.1% salicylic acid solution to prevent interference of alumina. The oxalate precipitate was then ignited to CaO. Alumina was determined in a fresh sample of the slag by addition of ammonium chloride and nitric acid to the HCl solution obtained as above and precipitation as hydrated hydroxide by the addition of ammonia at a pH of 6.5-7.5. The precipitate was redissolved in a little hot dilute hydrochloric acid, reprecipitated and ignited to alumina.

The master slags prepared gave the following analyses.

$CaO-Al_2O_3$ slags.	%CaO	$\%Al_2O_3$	Total
	41.1	58.6	99.7
	48.2	52.2	100.4
	54.4	45.8	100.2
$CaO-SiO_2$ slags.	%CaO	$\%SiO_2$	Total
	34.3	65.2	99.5
	55.4	45.1	100.5

Hence the accuracy of the slag analyses has been estimated at $\pm$1% of each constituent.

Estimation of Sulphur.

Three methods are available by which sulphur may be estimated in slags.

(1) gravimetrically, as barium sulphate;

(2) by evolution, as hydrogen sulphide, and

(3) by combustion, as sulphur dioxide.

On account of the small weight of samples used (0.2 - 0.4 gm), the low sulphur content of the slags (in some cases as low as 0.04%) and the time which would have been consumed by the gravimetric method, it was ruled out as impracticable. At the time when runs were being carried out on $CaO-Al_2O_3$ slags, estimation of the sulphur by evolution was considered to be more accurate than estimation by combustion (in oxygen) since in the latter only about 90% of the sulphur is evolved as SO_2, and an evolution method had just been published by Kitchener, Liberman and Spratt(48), for use with steels. This method claimed a satisfactory technique for 100% absorption of the hydrogen sulphide evolved in a combined absorption-oxidation medium, alkaline hypochlorite solution.

This method was then investigated to determine whether it was suitable for the estimation of sulphur in slags. The method for use with steels consisted of dissolving the sample in a fixed volume of 1.1 hydrochloric acid solution, in a stream of hydrogen and under slow heating. On complete solution of the sample, the solution was boiled for 5 minutes to ensure that all the hydrogen sulphide had been evolved and absorbed. The hydrogen sulphide was absorbed in alkaline N/10 hypochlorite solution, the absorbent was then boiled for 5 minutes to ensure complete

oxidation of colloidal sulphur and other sulphur compounds to sulphate, and titrated cold iodometrically against N/20 sodium thiosulphate solution. A condenser above the evolution flask ensured that no hydrochloric acid was carried over into the absorption flask. One other feature of the apparatus was that it was of all-glass construction - no rubber tubing was employed to ensure no loss of sulphide through absorption by the rubber, and all joints were of ground-glass. After the estimation of sulphur in the steel sample, a blank was carried out and the difference between the blank and the sample gave the sulphur content thus.

1 ml. N/20 thiosulphate $\equiv$ 0.2004 mgm. sulphur.

Various modifications in the procedure were found to be necessary in applying this method to slags.

(1) it was found that the slag samples required times of up to 1 hour's boiling before they were completely dissolved. Hence the vaseline which Kitchener et al used on the ground glass joints was replaced by a silicone stopcock grease which proved to be satisfactory in keeping the joints gas-tight.

(2) with slag samples of 0.2 gm. and less than 0.8% S, the N/10 sodium hypochlorite solution was replaced by N/40 hypochlorite, and N/80 sodium thiosulphate solution was used for the titration.

(3) the slag samples could not be powdered, since, in the case of the higher sulphur samples, there was a distinct smell of hydrogen sulphide when they were ground in the mortar. With the CaO-Al_2O_3 slags, this did not prove to be a difficulty since boiling the slags for a period of 10 - 60 minutes resulted in complete solution of the slag.

Some difficulty was experienced in obtaining consistent blanks. The blank titration was usually of the order of 40 ml. of thiosulphate. In several cases, however, low values for the blank titration were obtained. In investigating the reasons for this, several factors were checked, viz.,

(1) the effect of photosensitivity on the thiosulphate solution - this was shown to be negligible under the prevailing laboratory condition.

(2) the rate of flow of hydrogen through the apparatus - this was shown to have no effect, provided of course, that the rate of hydrogen flow was not sufficiently fast to carry over hydrochloric acid from the condenser into the alkaline hypochlorite solution. It was also checked that the hydrogen contained no hydrogen sulphide.

Up till that time, however, the apparatus had been rinsed out with acetone after each blank estimation. Occasionally the acetone was observed to contain a brown flocculent deposit, and it was shown that this was partially responsible for the errors in the blank - as, of course, was atmospheric dust of any description, but precautions had been taken against the latter. Also, at first the hydrochloric acid was stored in a Winchester bottle without any special precautions having been taken to prevent any contact with the atmosphere. However, it was found necessary to store it under nitrogen to prevent contact with air, since this was found to be a source of error in the blanks. With these precautions, nearly all the blanks were found to be within +0.3 ml. of the mean, while the majority of them were within $\pm$0.1 ml. of the mean.

A few blanks were outwith these limits and were rejected. The former limits gave ± 5% accuracy for slags of 0.15% sulphur using a 0.2 gm. sample, and proportionately better accuracies for slags of higher sulphur contents.

A fresh blast furnace slag of approximately 1% sulphur was used to determine the effect of other variables. The slag was powdered and kept in a sealed bottle to prevent oxidation of the sulphide. It was shown that, although the slag did not completely dissolve, consistent results were obtained provided it was boiled with the 1:1 acid for at least 1 hour. The effect of using different weights of sample was shown to be nil within the range 0.3 - 0.6 gms.

This method of analysis was found to be satisfactory for all $CaO-Al_2O_3$ slags and for a few $CaO-Al_2O_3-SiO_2$ slags (AS1-AS4). A gravimetric sulphate determination on a sample of the residual acid liquid containing the dissolved slag showed that no sulphate was present in the slag - which was to be expected from thermodynamic consideration.

In the case of $CaO-SiO_2$ slags, it was found that, since the slag would not dissolve in boiling 1:1 hydrochloric acid, the only way in which the evolution method could be used to ensure that all the sulphur was evolved was by grinding the slag and boiling it for at least 1 hour. However, as is noted above, there is a loss of sulphur on grinding. At this time, the combustion method of Fincham and Richardson (49) using carbon dioxide as the combusting gas, was published, and the sulphide contents of $CaO-SiO_2$ and of $CaO-Al_2O_3-SiO_2$ slags were estimated by this method. The slag pellet was not crushed but after the platinum

foil crucible had been peeled from it, was broken into about 4 smaller pieces and placed in a pre-ignited boat. The slag was combusted at 1450°C in a flow of carbon dioxide of about 1/4 l. per minute, the sulphur dioxide evolved was absorbed in a dilute hydrochloric acid solution containing starch and titrated during the combustion with an iodide-iodate solution (1 ml.≡ 0.1 mgm. sulphur). The time required for complete evolution of the sulphur varied from 30 to 120 minutes. Blank estimations also showed the necessity of making a slight correction, usually of the order of 0.1 ml. per 20 minutes of the time of evolution.

No absolute standardisation of the evolution method was possible, on account of there being no satisfactory standard sulphide available. However, a fresh blast-furnace slag (in which the sulphate sulphur should be negligible) was analysed by both the evolution and the combustion methods, the results obtained being as follows.

by evolution method	1.18% S.
by combustion method	1.21% S.

Therefore the evolution method can be considered as stoichiometric.

Experimental Procedure.

A number of preliminary runs were carried out on slag A6, using two 3/8 in. diameter crucibles, to ascertain whether equilibrium was being attained, and to ensure that certain variables did not affect the results.

On the evening prior to the day of a run, the reaction tray, crucibles and slag were placed in the furnace. The furnace tube was

tested to ensure that it was gas-tight, flushed out with nitrogen, then heated overnight to approximately 1000°C. A further 3 hours' heating the following morning brought it to 1500°C. During this period of heating the $CO-CO_2-SO_2$ gas mixture was run, by-passing the furnace, the bleeder columns being adjusted to give the desired rates of gas flow. Preliminary runs had shown that a gas of 0.8% SO_2 and $CO/CO_2 = 1.5$ would give sulphide contents of 0.13% S for slag A1 and c.1.2% S for slag A11, i.e., sulphur contents not too small for convenient analysis, nor sufficiently large to exceed the sulphur saturation value of the slag. Hence the gas flows were calculated to give that gas composition for a total flow of 150 ml. per minute. After running for at least an hour, the rates of flow of CO_2 and SO_2 were measured as previously described. When constant values were obtained, the gas sample collected at S was analysed for the $CO/(CO_2 + SO_2)$ ratio as previously described.

When the furnace was steady at the desired temperature the gas was flushed through the reaction tube, entering via the tube W (Fig.9) in the lower bung and leaving via the tube X in the upper bung. Flushing was complete in half-an-hour, after which the gas was led direct to the reaction chamber at the centre of the furnace tube via the alumina tube, V.

Various methods to determine when equilibrium had been attained were tried. Eventually the method adopted was to hold the slags for periods of $2\frac{1}{4}$, $3\frac{1}{4}$ and $4\frac{1}{4}$ hours. For all the slags used, exposure to the gas for a period of $3\frac{1}{4}$ hours was found to be adequate to ensure that equilibrium had been attained (as will be described below). At the end of this time the gas flow to the reaction chamber was cut off, the power

supply to the furnace switched off and the reaction tray immediately lowered a distance of about 3 ins. It was then slowly removed from the reaction tube over a period of 10 minutes to prevent spalling of either the tube or the tray. The slags were then analysed for sulphide in the manner described earlier in this Chapter.

Determination of the Attainment of Equilibrium.

The first means which, it was hoped, would indicate when equilibrium had been reached, was by the analysis of the exit gases from the reaction chamber. The reaction tube at that time incorporated an additional alumina tube, of the same bore as, and parallel to the gas entry tube V_3 by means of which the gas could be led immediately from the reaction chamber for sampling and analysis. This additional alumina tube led through a two-way stopcock to gas sampling bulbs in parallel, and then led into the common limb, Z, from which it could be led through limbs D and E for analysis for CO_2 and SO_2. The first attempt to use this method by the analysis of periodic samples of the exit gas for the ratio $CO/(CO_2+SO_2)$ was found to be impracticable because of the time consumed in carrying out the analysis. Following this, the rate of flow of sulphur dioxide in the exit gas was measured by absorption in hydrogen peroxide solution. The amount of sulphur dioxide present was found to be very small - about 2% of the quantity in the inlet gas - and also roughly constant. Thirdly, the weight of gas absorbed by soda-asbestos over a given time was tried, and proved more suitable for measurement. At 1500°C, carbon monoxide and sulphur dioxide react giving carbon dioxide

and various sulphur compounds. Accordingly, the weight of gas absorbed by soda-asbestos was found to be some 2-6% greater than that in the inlet gas. In some cases, it was found that there was a distinct maximum in the graph of weight flow absorbed in soda-asbestos per minute v. time, usually about 1-2 hours after the gas had first passed through the furnace, followed by a fall to a steady rate of flow. In other cases the graph rose to this steady value and no maximum was obtained. Further a blank run, in which no slags were used, was carried out, and the graph obtained for it showed a maximum after about an hour's running, followed by a fall to a steady value. Hence this method of indicating when equilibrium had been reached, by some kind of analysis of the exit gas, was abandoned as being unsatisfactory.

The second method of obtaining an indication of equilibrium was by the addition of sulphur to one of the two slag samples. In the first place, sulphur was added as calcium sulphide, an equivalent amount of alumina also being added to maintain the same $CaO:Al_2O_3$ ratio; this proved quite satisfactory, especially in run 4, (see Table V, p. 56) where a run of 3/4 hour's duration resulted in one slag, initially containing no sulphur, picking up 0.27% sulphur, while the other, containing initially 0.8% fell to 0.64% sulphur. Also, in run 8, of $3\frac{1}{4}$ hours duration slags of initial sulphur contents of 0.3 and 0.5% both gave analyses of 0.44% sulphur. Additions of calcium-sulphate were tried, but did not give satisfactory results and destroyed the platinum crucibles, appearing to cause embrittlement of the platinum. A further indication of the time required to attain equilibrium was obtained by carrying out a series of

runs, for increasing lengths of time, till constant results were obtained. Runs were carried out for periods of $2\frac{1}{4}$, $3\frac{1}{4}$ and $4\frac{1}{4}$ hours (See Table V, p. 56, runs 6, 7, 9 and 11). The results of runs 4-11 have been plotted against the duration of the run in Fig.10, and show that equilibrium was almost attained in $2\frac{1}{4}$ hours, and that $3\frac{1}{4}$ hours would be a sufficient time to ensure that equilibrium had been attained.

Similar runs for $3\frac{1}{4}$ and $4\frac{1}{4}$ hours were carried out on slags All, S1 and S6 (Table VI runs Nos.14-16, 31-32, 34-45). In each case, $3\frac{1}{4}$ hours was found to be adequate, for the attainment of equilibrium. It was assumed that this would hold for all the slag compositions used in the experiments. Hence all runs were carried out for a minimum duration of $3\frac{1}{4}$ hours.

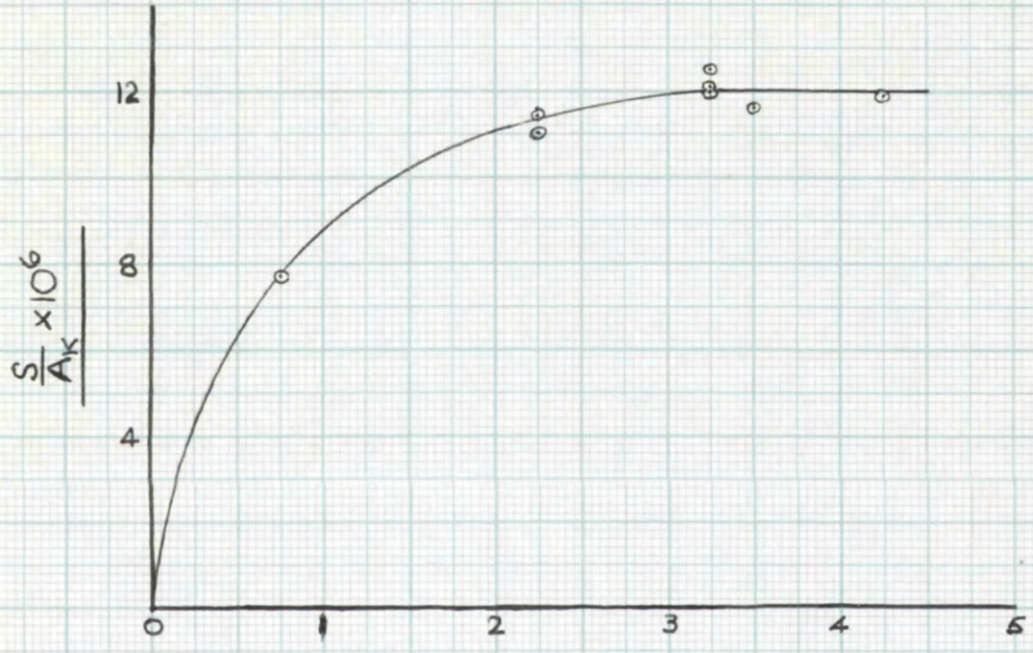


FIG. 10 : TIME REQUIRED FOR ATTAINMENT OF EQUILIBRIUM.

(USING SLAG A6)

CHAPTER V.

RESULTS OF SLAG-GAS EXPERIMENTS.

(1) Tables of Results.

Table IV shows the compositions of all the ratios $N_{CaO}/(N_{Al_2O_3}$ + ed in both weight per cent and mole fraction, their mole ratios $N_{CaO}/(N_{Al_2O_3}$ + N_{SiO_2}), and melting points. The melting points have been estimated from the binary and ternary diagrams collected by Hall and Insley(27) and given earlier (Figs. I, II, III,). The melting point of slag A12 is given as 1520°C. Although the run using this slag (run 22) was carried out at 1500°C as usual, examination of the slag after the run showed that the absorption of 1.6% sulphur had been sufficient to liquefy the slag completely at the experimental temperature. As will be shown later in Fig.11, the result obtained in this run fits the a_{CaO} v. %CaO graph for $CaO-Al_2O_3$ slags. In no other case was the liquidus temperature of the initial slag higher than the experimental temperature.

The results of the preliminary runs using slag A6 are shown in Table V. Table VI, shows the results of the runs using all other binary and ternary slags listed. All the data given refer to an experimental temperature of 1500°C (excepting runs 12 and 13), and to a total gas flow rate of 140-150 ml. per minute (excepting run 10). The estimation of sulphur in the slags in runs 1-25, 33, 41-44 and 88-89 was done by the evolution method, and the remaining slag sulphurs were estimated by combustion in carbon dioxide.

The values of the sulphurising potential of the gas, A, which have been used are those derived from Kelley's thermodynamic data, i.e., the A_K values. It will be shown later that Kelley's data are the data

TABLE IV.

COMPOSITIONS OF SLAGS.

No.	Composition (Wt.%) CaO	Al_2O_3	SiO_2	Mole Fractions N_{CaO}	$N_{Al_2O_3}$	N_{SiO_2}	Mole Ratio	Melting Point (°C)
CaO-Al_2O_3 Slags.							$N_{CaO}/N_{Al_2O_3}$	
A1	42.0	58.0	-	0.568	0.432	-	1.31	1500
A2	42.4	57.6	-	0.572	0.428	-	1.34	1490
A3	43.0	57.0	-	0.578	0.422	-	1.37	1480
A4	45.0	55.0	-	0.598	0.402	-	1.49	1450
A5	47.8	52.2	-	0.625	0.375	-	1.66	1450
A6	48.2	51.8	-	0.628	0.372	-	1.69	1450
A7	50.0	50.0	-	0.645	0.355	-	1.82	1400
A8	52.0	48.0	-	0.663	0.337	-	1.97	1430
A9	54.0	46.0	-	0.681	0.319	-	2.13	1460
A10	54.4	45.6	-	0.684	0.316	-	2.17	1470
A11	56.0	44.0	-	0.698	0.302	-	2.31	1490
A12	58.0	42.0	-	0.715	0.285	-	2.51	1520
CaO-SiO_2 Slags.							N_{CaO}/N_{SiO_2}	
S1	35.0	-	65.0	0.366	-	0.634	0.58	1500
S2	38.0	-	62.0	0.395	-	0.605	0.65	1450
S3	42.5	-	57.5	0.442	-	0.558	0.79	1500
S4	52.0	-	48.0	0.537	-	0.463	1.16	1500
S5	53.0	-	47.0	0.547	-	0.453	1.21	1490
S6	55.4	-	44.6	0.571	-	0.429	1.33	1470
S7	56.0	-	44.0	0.577	-	0.423	1.36	1500
CaO-Al_2O_3-SiO_2 Slags.							$N_{CaO}/(N_{Al_2O_3}+N_{SiO_2})$	
AS1	60.5	32.5	7.0	0.713	0.210	0.077	1.77	1500
AS2	57.2	39.8	3.0	0.698	0.268	0.034	2.31	1480
AS3	58.3	35.7	6.0	0.698	0.235	0.067	2.31	1460
AS4	59.5	31.5	9.0	0.698	0.203	0.099	2.31	1490
AS5	56.3	39.0	4.7	0.686	0.261	0.053	2.04	1450
AS6	53.4	35.3	11.3	0.640	0.233	0.127	1.98	1500
AS7	49.0	34.0	17.0	0.586	0.224	0.190	1.42	1500
AS8	47.2	38.8	14.0	0.578	0.262	0.160	1.37	1490
AS9	49.3	40.7	10.0	0.609	0.276	0.115	1.55	1400
AS10	42.5	46.7	10.8	0.543	0.328	0.129	1.19	1500
AS11	44.5	48.5	7.0	0.573	0.343	0.084	1.22	1460

TABLE IV. (Cont'd).

COMPOSITIONS OF SLAGS.

No.	Composition (Wt.%)			Mole Fractions			Mole Ratio	Melting Point (°C)
	CaO	Al_2O_3	SiO_2	N_{CaO}	$N_{Al_2O_3}$	N_{SiO_2}	$N_{CaO}/N_{Al_2O_3}+N_{SiO_2}$	
$CaO-Al_2O_3-SiO_2$ Slags.								
AS12	46.0	50.0	4.0	0.596	0.356	0.048	1.47	1430
AS13	51.8	5.0	43.2	0.546	0.029	0.425	1.20	1400
AS14	50.7	10.0	39.3	0.546	0.059	0.395	1.20	1440
AS15	49.6	15.0	35.4	0.546	0.091	0.363	1.20	1470
AS16	38.0	4.0	58.0	0.403	0.023	0.574	0.67	1450
AS17	38.0	8.0	54.0	0.410	0.047	0.543	0.69	1430
AS18	38.0	12.0	50.0	0.416	0.072	0.512	0.71	1390
AS19	38.0	16.0	46.0	0.423	0.098	0.479	0.73	1330
AS20	38.0	20.0	42.0	0.431	0.125	0.444	0.76	1270
AS21	38.0	23.0	39.0	0.437	0.145	0.418	0.78	1370
AS22	38.0	26.0	36.0	0.442	0.167	0.391	0.79	1430
AS23	38.0	30.0	32.0	0.450	0.196	0.354	0.82	1490
AS24	40.0	10.0	50.0	0.434	0.060	0.506	0.77	1420
AS25	40.0	14.0	46.0	0.441	0.085	0.474	0.79	1360
AS26	40.0	18.0	42.0	0.449	0.111	0.440	0.81	1290
AS27	40.0	22.0	38.0	0.457	0.138	0.405	0.84	1410
AS28	40.0	23.0	37.0	0.459	0.145	0.396	0.85	1430
AS29	40.0	26.0	34.0	0.465	0.166	0.369	0.87	1490
AS30	45.5	3.8	50.7	0.479	0.022	0.499	0.92	1500
AS31	45.1	7.5	47.4	0.482	0.044	0.474	0.93	1450
AS32	44.8	11.3	43.9	0.487	0.068	0.445	0.91	1370
AS33	44.3	15.1	40.6	0.490	0.091	0.419	0.96	1340
AS34	43.7	20.5	35.8	0.494	0.128	0.378	0.96	1470
AS35	46.0	5.0	49.0	0.487	0.029	0.484	0.95	1490
AS36	46.0	8.7	45.3	0.494	0.051	0.455	0.98	1420
AS37	46.0	12.4	41.6	0.503	0.074	0.423	1.01	1330
AS38	46.1	16.5	37.4	0.512	0.101	0.387	1.05	1430
AS39	52.0	3.3	44.7	0.544	0.019	0.437	1.20	1440
AS40	52.0	6.6	41.4	0.551	0.039	0.410	1.23	1430
AS41	50.0	10.0	40.0	0.539	0.059	0.402	1.19	1380
AS42	31.6	45.5	22.9	0.405	0.321	0.274	0.68	1500

TABLE V.

RESULTS OF PRELIMINARY RUNS ON SLAG A6.

(Unless otherwise stated, runs are at 1500°C and 140-150 ml.per minute).

Run No.	Inlet Gas CO/CO_2	Inlet Gas $\%SO_2$	Inlet Gas A_K	Time of Run (hrs.)	SLAG %S	SLAG Glass G	SLAG Mean % S.	$\frac{S}{A_K} \times 10^6$	Remarks.
1.	1.51	0.78	340	4	1)0.408 2)0.408	G	0.408	12.0	
2.	1.50	0.77	330	4	1)0.428 2)0.400		0.414	12.6	Furnace-cooled.
3.	1.51	0.77	334	3½	1)0.318 2)0.320		0.319	9.6	Delayed quench.
4.	1.52	0.83	356	¾	1)0.275 2)0.640				Neither at equilibrium. 0.8%S added to(2).
5.	1.51	0.79	340	2¼	1)0.396 2)0.378		0.387	11.4	Almost at equilibrium Narrow gas-tube.
6.	1.48	0.82	340	2¼	1)0.394 2)0.363	G	0.378	11.1	Almost at equilibrium.
7.	1.52	0.83	357	3¼	0.446	G		12.5	No duplicate.
8.	1.55	0.84	367	3¼	1)0.439 2)0.439	G G	0.439	12.0	0.3%S added to(1) 0.5%S added to(2).
9.	1.49	0.83	346	3¼	0.417	G		12.1	No duplicate.
10.	1.47	0.82	336	3½	1)0.391 2)0.388	G G	0.390	11.6	65ml./min.gas flow.
11.	1.49	0.84	348	4¼	1)0.401 2)0.423		0.412	11.9	
12.	1.50	0.85		3¼	0.372	G			At 1513°C, no duplicate
13.	1.50	0.86		3¼	1)0.332 2)0.371		0.352		At 1525°C

Mean value of $S/A_K \times 10^6$ (from runs 7-11) is 12.0.

TABLE VI.

RESULTS OF ALL SLAGS.

(Unless otherwise stated, all runs are of $3\frac{1}{4}$ hours' duration).

Run No.	Slag No.	Inlet Gas CO/CO_2	Inlet Gas $\%SO_2$	A_K	SLAG %S	SLAG GLASS G	$S/A_K(\times10^6)$ VALUE	$S/A_K(\times10^6)$ MEAN VALUE	a_{CaO_K}
7-11	A6							12.0	0.23
14	A11	1.52	0.80	347	1.25		36.0		
15**	A11	1.49	0.85	349	1.29		37.0	36.5	0.69
16*	A11	1.51	0.78	337	1.23		36.4		
17	A1	1.52	0.80	347	1)0.137	G	3.95	3.92	0.074
					2)0.135	G	3.89		
18	A4	1.52	0.83	356	0.232		6.5		0.123
19	A7	1.52	0.83	356	0.570		16.0		0.305
20	A8	1.50	0.83	351	1)0.304		22.9	22.9	0.44
					2)0.804		22.9		
21	A9	1.50	0.86	358	1.02		28.4		0.54
22	A12	1.50	0.86	358	1)1.65		46.1	44.8	0.85
					2)1.55		43.4		
23	AS1	1.52	0.77	340	1)1.81		53.3	52.7	1.00
					2)1.77		52.1		
24	A2	3.32	2.83	1600	0.571		3.56	3.66	0.069
25	A2	3.36	3.18	1680	0.631		3.76		
26	A3	1.49	0.72	311	0.147	G	4.73		0.090
27	A5	1.06	0.72	168	0.196	G	11.7		0.222
28	A5	1.51	0.30	165	0.196	G	11.9		0.226
29	A10	1.06	0.72	168	0.46	G	27.2		0.52
30	AS1	1.06	0.72	168	0.88	G	52.4		0.99
31	S1	3.67	3.08	1800	1)0.040	G	0.22		
					2)0.036	G	0.20		
32*	S1	3.69	3.02	1800	1)0.036	G	0.20	0.21	0.0040
					2)0.039	G	0.21		
33	S6	1.51	0.82	349	0.064		1.83		0.035
34	S6	3.67	3.08	1800	1)0.318		1.76	1.73	0.033
					2)0.333		1.84		
35*	S6	3.69	3.02	1800	1)0.305		1.70		
					2)0.291		1.62		
36	S2	3.71	2.90	1790	0.030	G	0.17		0.0032
37	S3	3.62	3.11	1780	1)0.045		0.25	0.27	0.0051
					2)0.050		0.28		
38	S4	4.70	3.41	2260	0.259	G	1.15		0.022
39	S5	3.62	3.11	1780	1)0.262	G	1.47	1.45	0.028
					2)0.256	G	1.43		
40	S7	4.53	3.13	2160	0.348	G	1.61		0.031
41	AS2	1.52	0.86	365	1.40		38.4	38.5	0.73
42	AS2	1.51	0.84	355	1.36		38.5		

** $3\frac{3}{4}$ hours' run. * $4\frac{1}{4}$ hours' run.

TABLE VI. (Cont'd).

Run No.	Slag No.	INLET GAS CO/CO_2	INLET GAS $\%SO_2$	INLET GAS A_K	SLAG $\%S$	SLAG GLASS G	$S/A_K(\times10^6)$ VALUE	$S/A_K(\times10^6)$ MEAN VALUE	a_{CaO_K}
43	AS3	1.51	0.84	355	1) 1.53		43.2	44.2	0.84
					2) 1.60		45.2		
44	AS4	1.52	0.84	358	1) 1.53		42.8	44.0	0.84
					2) 1.62		45.2		
45	AS5	1.43	0.98	361	1.04		28.8		0.55
46	AS6	1.43	0.98	361	0.462		12.8		0.245
47	AS7	1.49	0.72	311	0.153		4.92		0.093
48	AS8	1.43	0.98	361	0.124		3.44		0.065
49	AS9	1.37	0.88	311	0.314	G	10.1		0.192
50	AS10	1.48	0.49	236	0.092	G	3.90		0.074
51	AS11	1.37	0.88	311	0.189	G	6.07		0.115
52	AS12	1.37	0.88	311	0.192	G	6.17		0.117
53	AS13	3.62	3.05	1770	1) 0.314	G	1.77	1.85	0.035
					2) 0.341	G	1.92		
54	AS14	3.62	3.05	1770	1) 0.407	G	2.29	2.24	0.042
					2) 0.387	G	2.18		
55	AS15	3.32	2.83	1600	1) 0.462		2.88	2.83	0.054
					2) 0.444		2.77		
56	AS16	3.71	2.90	1790	0.038	G	0.21		0.0040
57	AS17	3.88	2.66	1810	0.044	G	0.24	0.22	0.0042
58	AS17	3.71	2.90	1790	0.036	G	0.20		
59	AS18	4.64	3.17	2200	0.083	G	0.38	0.38	0.0072
60	AS18	3.58	2.89	1730	0.066	G	0.38		
61	AS19	3.58	2.89	1730	0.069	G	0.40		0.0076
62	AS20	3.69	2.61	1720	1) 0.074	G	0.43	0.47	0.0089
					2) 0.089	G	0.51		
63	AS21	3.88	2.66	1810	1) 0.077	G	0.42		
					2) 0.069	G	0.38	0.48	0.0091
64	AS21	3.58	2.89	1730	0.111	G	0.64		
65	AS22	3.58	2.89	1730	0.093	G	0.57		0.0108
66	AS23	3.69	2.61	1720	1) 0.124	G	0.72	0.71	0.0135
					2) 0.121	G	0.70		
67	AS24	3.71	2.90	1790	0.053	G	0.29		0.0055
68	AS25	3.74	2.87	1800	0.052	G	0.29		0.0055
69	AS26	3.74	2.87	1800	0.079	G	0.44		0.0084
70	AS27	3.74	2.87	1800	0.104	G	0.57		0.0108
71	AS28	3.88	2.66	1810	0.107	G	0.59		0.0112
72	AS29	3.74	2.87	1800	0.103	G	0.57	0.79	0.0150
73	AS29	4.64	3.17	2200	0.219	G	1.00		
74	AS30	4.39	3.41	2140	0.120	G	0.56	0.53	0.0101
75	AS30	4.05	3.07	1960	0.096	G	0.49		
76	AS31	4.05	3.07	1960	0.124	G	0.63		0.0120

TABLE VI. (Cont'd).

Run No.	Slag No.	INLET GAS CO/CO_2	INLET GAS $\%SO_2$	INLET GAS A_K	SLAGS %S	SLAGS GLASS G	$S/A_K(\times10^6)$ VALUE	$S/A_K(\times10^6)$ MEAN VALUE	a_{CaO_K}
77	AS32	4.05	3.07	1960	0.159	G	0.81		0.0154
78	AS33	4.53	3.13	2160	0.225	G	1.04		0.0197
79	AS34	4.05	3.07	1960	0.192	G	0.98		0.0186
80	AS35	4.76	2.92	2210	1) 0.139	G	0.63)		
					2) 0.146	G	0.66)	0.65	0.0123
81	AS36	4.53	3.13	2160	0.182	G	0.84		0.0159
82	AS37	4.39	3.41	2140	0.229	G	1.07		0.020
83	AS38	4.76	2.92	2210	0.309	G	1.40		0.027
84	AS39	4.70	3.41	2260	0.324	G	1.43		0.027
85	AS40	4.70	3.41	2260	0.424	G	1.88		0.036
86	AS41	4.64	3.17	2200	0.422	G	1.92		0.036
87	AS42	4.39	3.41	2140	0.126	G	0.59		0.0112
Runs not used in calculations of activities.									
88	A10	3.22	0.95	980	1) 4.5		46		
					2) 6.1		62		
	Expected value at 980.				2.9		29.8		0.566
89	AS6	3.70	2.90	1780	2.52		14.2		
	Expected value						12.8		

Sulphur analyses of runs 1-25, 33, 41-44 and 88-89 were carried out by the evolution method, and of all other runs by the combustion method.

which agree best with the results obtained in the present work. Column 9 of Table V, and column 8 of Table VI, show the value of the ratio S/A_K for each run. This ratio is proportional to the activity of CaO in the slag, hence S/A_K values for runs 7-11 (all using slag A6) should be constant - which was found to be the case. In run 23, the standard slag AS1 ($a_{CaO} = 1.00$) was used and the value of 52.7×10^{-6} obtained for S/A_K for this slag. The activity of each slag, shown in column 10, was calculated using this value, and is denoted by a_{CaO_K}.

The S/A_K value for each individual sample has been shown in the Tables. For most of the binary slags, duplicate samples were used. Where no duplicate result is shown, it infers in most cases that the duplicate sample was lost - usually on account of leakage of the crucible. For most of the ternary slags, only one sample of each composition was used. Occasionally, however, duplicates of samples were carried out, sometimes using different gas compositions. Where duplicates have been carried out, only the mean value of a_{CaO} has been calculated.

The agreement obtained between duplicates was reasonably good. Examination of the results using slag A6 (runs 7-11) shows that all lie within $\pm 5\%$ of the mean. Over the other duplicates, agreement in all but two cases was within $\pm 10\%$ - which is regarded as satisfactory, since in many cases the sulphur content of the slags was less than 0.1%. Two other points may be noted here. (1) the sulphur content of the slags was never greater than 1.8%, and in more than 80% of the runs the sulphur content was less than 0.5%. (2) the appearance of the slags varied considerably, the majority were glasses, white, clear or yellow in colour,

whilst the others were minutely crystalline, white, greyish or yellow in colour. Two slags (AS7 and S6) were "falling slags" and became powders on standing for a day or two. In the columns in Tables V and VI headed "Glass", glassy slags are indicated by "G" and unmarked slags are minutely crystalline. No relation could be seen between the colour and the tendency to glass formation of a slag on the one hand, and its composition on the other, and it is probable that variations in appearance - which were obtained even between duplicates of the same slag in the same run - are to be explained by slight differences in the cooling of slag samples on completion of a run.

(2) Preliminary Runs Using Slag A6 - Table V.

These preliminary runs were designed to show the effect of certain variables on the results obtained, as follows:

(a) Effect of Rate of Cooling.

The difference between the normal method of cooling of slags, as described on p.50 , and furnace-cooling is shown by runs 1 and 2. At the end of run 2, after the gas flow and power supply had been cut off, the slag samples were allowed to cool within the furnace hot zone. Comparison with run 1 shows the furnace-cooled samples to be about 5% higher. Under furnace cooling the sulphur content of the slag tends towards the equilibrium sulphur content of the slag at the temperature of solidification. It would appear, therefore, that the sulphur content of the slag in equilibrium with a gas of given initial composition

increases with fall in temperature. Subsequently all slags were cooled to give rapid solidification by lowering the reaction tray 3 ins. immediately after terminating a run.

(b) Effect of the reaction tray sticking in the furnace tube.

At the end of a run it was occasionally found, after the lower bung and stools had been removed, that the reaction tray had stuck in the centre of the furnace tube - due to canting for instance. Run 3 ("delayed quench") was such an instance, and the result shows that atmospheric oxygen had reacted with some of the sulphur before solidification had taken place, giving a low result. Hence all such runs were discarded.

(c) Effect of Changes in the Rate of Gas Flow.

This is shown by runs 5 and 10. In run 5 the gas mixture entered the reaction chamber via an alumina tube, V, (Fig.9) of narrower bore - $\frac{1}{16}$ in. internal diameter instead of the normal $\frac{1}{8}$ in. Since the total gas flow was maintained at 150 mls. per minute, the linear gas velocity down the entry was four times as great. The result of run 5 is seen to be comparable to that of run 6, both being for $2\frac{1}{4}$ hours, i.e., equilibrium very nearly, but not quite, attained. The change in linear gas velocity has made no significant difference to the result. In run 10 the total gas flow was reduced to 65 mls. per minute. Again no significant difference is seen in the result. It can, therefore, be inferred that the gas is adequately preheated before reaching the reaction chamber, and that errors due to thermal diffusion or to incomplete attainment of

equilibrium in the gas mixture are within the limits of experimental error.

(d) The effect of temperature.

Runs 12 and 13 were carried out at 1513°C and 1525°C respectively If run 12 had been conducted at 1500°C, the A_K value of the gas would have been 354, and, since the mean value of S/A_K for slag A6 is 12.0 x 10^{-6}, a slag sulphur of 0.425% would have been obtained. Therefore, a rise in temperature of 13°C, giving 0.372% S, results in a loss of 13% of the sulphur content. Similarly run 13 would have given an A_K of 356 and a slag of 0.427% S at 1500°C. Therefore, a rise in temperature of 25°C results in a loss of 18% of the sulphur content. Therefore, the sulphur content of a slag in equilibrium with a gas of given initial composition decreases with rise in temperature, the rate for slag A6 being approximately 1% of the sulphur content per °C at 1500°C. This confirms the qualitative conclusion reached above from the furnace-cooled sample.

At first sight this appears to contradict the results of Fincham and Richardson(15) who showed that, under gases of constant equilibrium p_{O_2} and constant SO_2 input, raising the temperature increases the amount of sulphur in the melt. At different temperatures gases of the same initial SO_2 content and of the same equilibrium p_{O_2} are initially of different compositions. Therefore, the results of the present work cannot be compared directly with those of Fincham and Richardson. To facilitate comparison it is necessary to recalculate the results of the present work and thus obtain the effect of changes in temperature on the absorption of sulphur by slag A6 under gases of the same initial SO_2

content and equilibrium p_{O_2}. This was carried out for the results of run 12 as follows.

By extrapolation of the data for 1510°C in the Appendix, calculations numbers 127-8, it can be shown that at 1513°C, a gas of initial CO/CO_2 = 1·50 and SO_2 = 0·85% gives A_K = 298 and $p_{O_2} = 1{\cdot}62 \times 10^{-8}$. Slag A6 absorbed 0·372% S from this gas at 1513°C (result of run 12).

At 1500°C a gas of the same initial SO_2 content (0·85%) and of the same equilibrium p_{O_2} ($1{\cdot}62 \times 10^{-8}$) gives A_K = 282 and its initial CO/CO_2 = 1·31. From the S/A_K value of slag A6 at 1500°C, it can be shown that, at equilibrium with this latter gas, slag A6 would have absorbed 0·339% S. Therefore, a rise of 13°C, using gases of constant initial SO_2 content and equilibrium p_{O_2} results in a change in sulphur content from 0·339% to 0·372%, i.e., a rise of $\frac{3}{4}$% per °C., which agrees qualitatively with the conclusion of Fincham and Richardson.

It will be seen from the later discussion (p.80) that whether a_{CaO} rises or falls with increase in temperature depends on the composition of the slag. For slag A6, the effect of temperature on the a_{CaO} value can be determined as follows. For the reaction

$$CaO_{(s)} + \tfrac{1}{2}S_2 = CaS_{(s)} + \tfrac{1}{2}O_2 \quad \ldots\ldots\ldots \quad (3)$$

$$K = \frac{a_{CaS}}{a_{CaO}.A_K}$$

Equilibrating slag A6 with the same initial gas at 1500°C and 1513°C, it follows that

$$\frac{a_{CaO(1500°C)}}{a_{CaO(1513°C)}} = \frac{S_{1500°C}}{S_{1513°C}} \cdot \frac{A_{K(1500°C)}}{A_{K(1513°C)}} \cdot \frac{K_{1513°C}}{K_{1500°C}} \cdot \frac{\gamma_{1500°C}}{\gamma_{1513°C}}$$

In calculating the effect of temperature on A_K, it was shown (p.31), that the rate of change of A_K for a given gas was -1·3% per °C. The present work shows that, for a given initial gas, the sulphur content of the slag decreases by approximately 1% per °C. The values of $K_{1500°C}$ and $K_{1513°C}$ can be obtained from the free energy equation for the reaction (3) above. Rosenqvist(32) has shown that the free energy for the reaction

$$CaO_{(s)} + H_2S = CaS_{(s)} + H_2O$$

is given by

$$\Delta G^\circ_T = -15,560 + 0·87T$$

Combining this with the free energy given by Richardson and Jeffes(34) for

$$H_2 + \tfrac{1}{2}O_2 = H_2O$$

$$\Delta G^\circ_T = -59,000 + 13·38T$$

and the free energy given by Richardson and Jeffes (36), for

$$H_2 + \tfrac{1}{2}S_2 = H_2S$$

$$\Delta G^\circ_T = -21,580 + 11·81T,$$

the free energy equation for the reaction (3) above is given by

$$\Delta G^\circ_T = +21,770 - 0·70T$$

$\therefore$ $K_{1500°C} = 2·94 \times 10^{-3}$ and $K_{1513°C} = 3·08 \times 10^{-3}$

$\therefore$ $\dfrac{a_{CaO(1500°C)}}{a_{CaO(1513°C)}} = \dfrac{1}{0·87}\ \dfrac{0·83}{1} \cdot \dfrac{1·047}{1} \cdot \dfrac{\gamma_{1500°C}}{\gamma_{1513°C}} = 0·999\,\dfrac{\gamma_{1500°C}}{\gamma_{1513°C}}$

If γ_{CaS} remains constant, then a_{CaO} will not vary within the temperature range 1500° - 1513°C. As the solubility of CaS probably rises with temperature an accompanying decrease in γ_{CaS} might be expected. For this particular slag this would therefore indicate a decrease in a_{CaO} with rise in temperature.

(3) The $CaO-Al_2O_3$ System.

The a_{CaO_K} values of $CaO-Al_2O_3$ slags and of the standard slag AS1 obtained using gases of approximately constant A_K values of 350 ± 15 (run 7-22) were plotted against wt.% CaO as shown in Fig.11, (points without appended numbers). The smooth curve obtained shows a steady increase of a_{CaO} with % CaO until unit activity is reached at approximately 59% CaO. This agrees well with the value of 59% CaO obtained for the point at which the extrapolated CaO liquidus cuts the 1500°C isotherm (Fig.1).

On account of the large differences between the calculated values of A_K and A_R for a given gas, it was originally intended to circumvent the resulting difficulty by equilibrating all slags under gases of approximately constant composition. However, when $CaO-SiO_2$ slags were equilibrated with gases of A_K values of 350 ± 15, it was found that even with slag S6, i.e., almost the highest CaO content possible in a $CaO-SiO_2$ slag liquid at 1500°C, the sulphur content obtained was only 0.064% (run 33). It was therefore necessary to use gases of higher sulphurising potentials, e.g., A_K = 1600-2200. Accordingly before further runs were carried out using $CaO-SiO_2$ slags, it was necessary to obtain data from which a decision could be made as to whether the A_K or the A_R gas values were the more accurate. It would have been ideal if gases of the higher sulphurising potentials could have been equilibrated with the standard slag AS1, but this was impracticable since the quantity of sulphur absorbed would have been 8-10%. Slag S6 had been equilibrated with a gas of low sulphurising potential (run 33) and was later

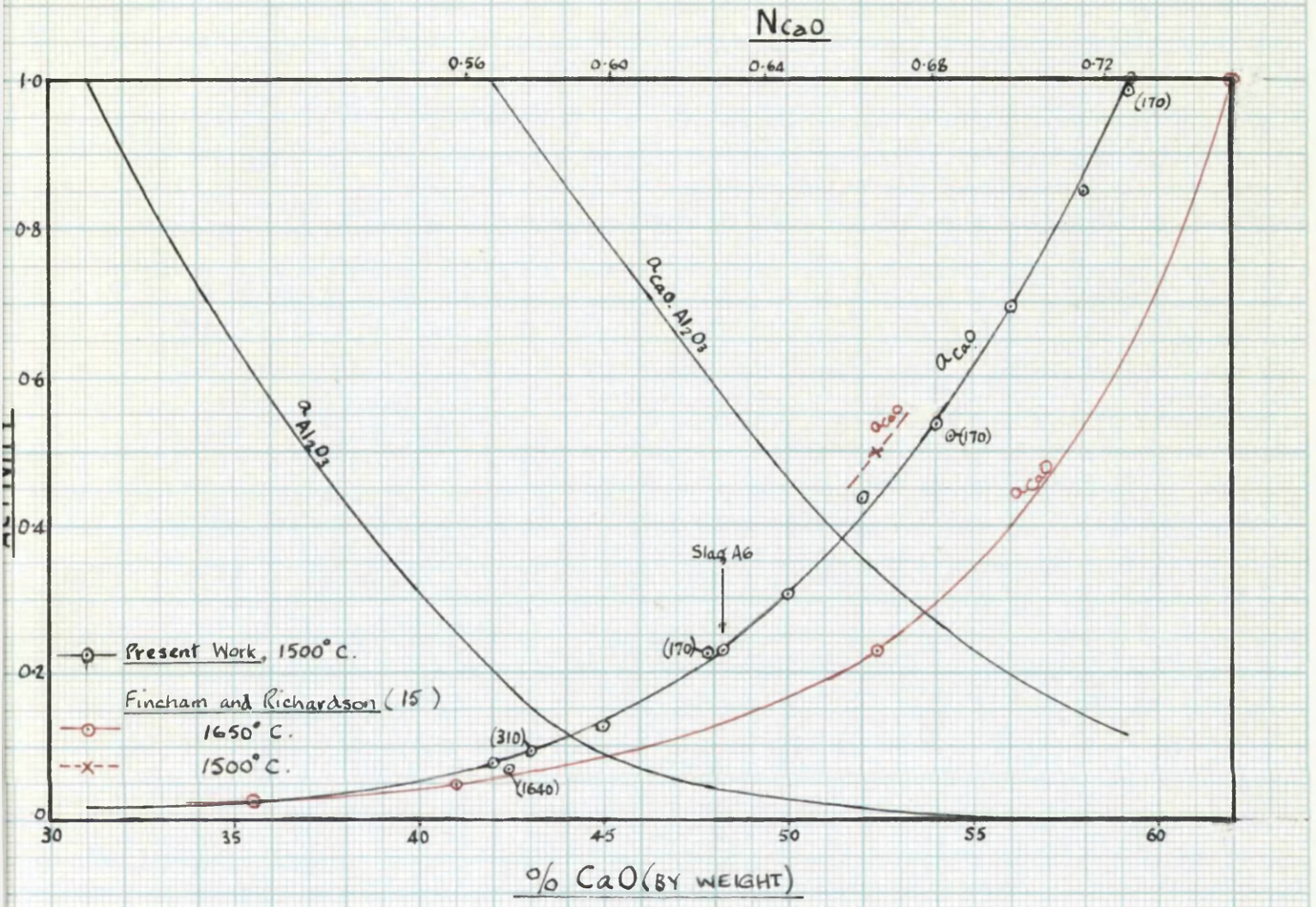


FIG. 11: ACTIVITIES IN $CaO-Al_2O_3$ SLAGS.

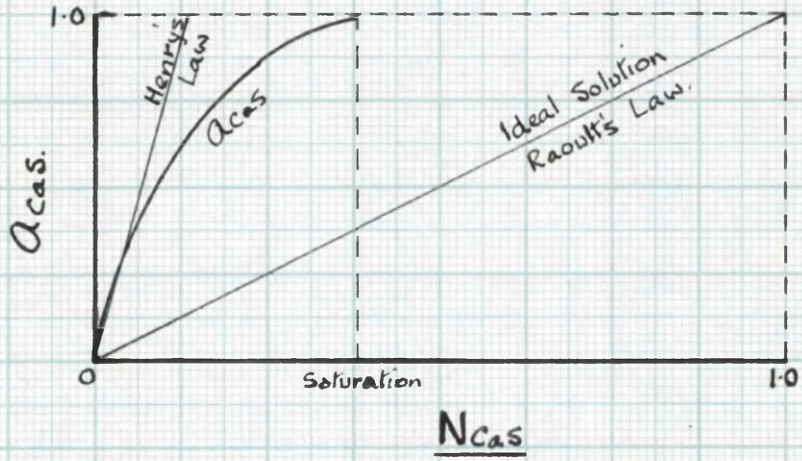


FIG. 12: TYPICAL ACTIVITY-MOLE FRACTION CURVE.

FOR A SOLUTION OF CaS IN A SLAG.

equilibrated with gases of high sulphurising potentials (runs 34 and 35). When the A_K values are used, it can be seen, from Table VI, that S/A_K is approximately constant for the three runs. On Fig.13, the result of run 33 is shown separately from the mean of runs 34 and 35 (A_K values are appended to both points). If the A_R values had been used, the following results would have been obtained.

Run 33 : $A_R = 180$ $S = 0.064\%$ $S/A_R = 3.6 \times 10^{-6}$ $a_{CaO_R} = 0.035$

Mean of Runs 34 and 35 : $A_R = 1430$ $S = 0.326\%$ $S/A_R = 2.3 \times 10^{-6}$ $a_{CaO_R} = 0.022$

These two a_{CaO_R} values have also been shown on Fig.13, (with A_R values appended). It can be seen that, while the a_{CaO_R} value of run 33 must be the same as the a_{CaO_K} value, the a_{CaO_R} value of runs 34 and 35 drops to about 65% of the corresponding a_{CaO_K} value. Although this indicates that the A_K values are more accurate, it was felt that no great stress could be put on this result since the accuracy of the slag sulphur analysis in run 33 (in which the sulphur was estimated by the evolution method) was about $\pm$ 25%, on account of the low titration difference of 1.2 mls., equivalent to the sulphur content. Therefore, some better method of comparison was required.

In Chapter III, p.27, values of A which have been calculated using the various free energy data available, are shown for two gases of widely different sulphurising potentials, (1) of initial CO/CO_2 of 1.52 and initial SO_2 of 0.81%, and (2) of initial CO/CO_2 of 3.34 and initial SO_2 of 3.01%. From these, values of the ratio A_2/A_1 were calculated and compared as shown in Table II. Using the data of

Richardson and Jeffes(36), A_2/A_1 = 7.07, using the data of Chipman and St. Pierre(41), A_2/A_1 = approximately 6.4; and using the data of Kelley(35), A_2/A_1 = 4.69. It was also pointed out that, by bringing samples of the same slag to equilibrium with gases(1) and (2), an experimental value of the ratio $A_2/A_1 = S_2/S_1$ would be obtained, where S_1 and S_2 are the sulphur contents of the slag at equilibrium with gases (1) and (2) respectively.

A $CaO-Al_2O_3$ slag of low CaO content, slag A2, was selected for this comparison, in order to keep the %S absorbed by the slag when equilibrated with the gas of higher sulphurising potential under the limit of 2%. Runs 24 and 25 show the results obtained using the gas of higher sulphurising potential.

For the standard slag, $S/A_K = 52.7 \times 10^{-6}$. Since $a_{CaO} \propto S/A_K$, it can be shown from Fig.11, that for slag A2,

$$S_1/A_{K_1} = 4.16 \times 10^{-6}$$

$\therefore$ at $A_{K_1} = 350$, $S_1 = 0.146\%S$.

From runs 24 and 25,

$$\text{at } A_{K_2} = 1640, \quad S_2 = 0.601\%S$$

$\therefore$ $S_2/S_1 = 4.12$.

Comparing this with the values of the ratio A_2/A_1 given above, obtained using the free energy data of Richardson and Jeffes(36), of Chipman and St. Pierre(41) and of Kelley(35), it can be seen that the experimental data fit the free energy data of Kelley more closely than they do any of the other free energy data. The experimental evidence given thus

supports the values of +101 and +119.5 kcals. for the dissociation energies of S_2 and SO respectively. This conclusion, however, is based on the results of experimental work on one slag composition and a number of similar experiments should be carried out before the above findings can be regarded as conclusive. In the present work calculations of experimental results are based on the A_K values of the gases, but where the use of A_R values produce significant differences, the results based on the A_R values are also shown, these results being denoted by the suffix R.

In the above calculation, an error will be introduced if there is any significant difference between the values of γ_{CaS} at 0.146% S and at 0.60%S. The direction of such an error can be shown as follows. The activity-mole fraction curve of a solution of CaS in a slag will probably take a form similar to that shown diagrammatically in Fig.12. This is similar in form to the approximate curve for the activity of CaS in blast furnace slags derived by Rosenqvist(32) from the experimental data of Hatch and Chipman(33), shown in Fig.4. Such a curve shows positive deviations from Raoult's Law but negative deviations from Henry's Law. γ_{CaS} is given by the slope of the chord of the curve and decreases with increase in the sulphur content of the slag. In the case of the slags of sulphur contents S_1 (0.146%S) and S_2 (0.60%S) above,

$$\gamma_{CaS}' > \gamma_{CaS}''$$

where γ_{CaS}', γ_{CaS}'' refer to the activity coefficients of CaS in the A2 slags containing S_1 and S_2% sulphur respectively. Further, where N'_{CaS}, N''_{CaS} and a'_{CaS}, a''_{CaS} refer similarly to the mole fractions and activities of CaS respectively in the two slags, then

$$\frac{A_2}{A_1} = \frac{a_{CaO}''}{a_{CaS}'} = \frac{\gamma_{CaS}'' \cdot N_{CaO}''}{\gamma_{CaS}' \cdot N_{CaS}'} = \frac{\gamma_{CaS}''}{\gamma_{CaS}'} \cdot \frac{S_2}{S_1}$$

In the calculation above to decide which thermodynamic data fit best, it was assumed that γ_{CaS} was constant for the range of slag sulphur contents used, i.e., that $A_2/A_1 = S_2/S_1$. The correction for the error introduced by this assumption would therefore decrease the value of the ratio a_{CaS}''/a_{CaS}' i.e., in this particular case, the value of $S_2/S_1 = 4.12$ would tend to be decreased if allowance were made for the variation in the value of γ_{CaS}. Such a correction would therefore not alter the decision regarding the various sets of free energy data.

One other source of possible error lies in the use of slags of the same initial composition for the comparison, no compensation being made for the effect of the replacement of some oxide by sulphide in the experiment. The results of Fincham and Richardson(15) which show that a_{CaS} is proportional to %S from 0.003 to 1.3% S in their slags (see above, p.20) suggest that this error is negligible.

It has been shown above that the experimentally determined ratio $S_2/S_1 = 4.12$, and that the ratio A_2/A_1 obtained using the data of Kelley is 4.69. This discrepancy may be due to (a) inaccuracies in the thermodynamic data used by Kelley, as well as to (b) experimental errors in determining S_2/S_1. It it was assumed that the error was due

totally to (a), and that the value of A_K = 350 was the true A value of the gas of composition (1) above, then the correction factor (based on the experimental data) which would require to be applied to the A_K value of 1640 to obtain the true A value would be 4.12/4.69 = 0.88, i.e., the true A value of the gas of composition (2) would be 12% lower than the value given by the A_K graph for this gas. In several runs (Nos.26-30) various CaO-Al_2O_3 slags were equilibrated with gases of A_K values less than 350. The results of these runs are also plotted on Fig.11, the numbers appended to the points on the graph indicating the A_K values of the gases used (no correction being applied to these A_K values). An examination of these points shows that they all lie, within the probable limits of experimental error, on the curve and, moreover, that the point obtained from runs 24 and 25, using the gas of A_K = 1640, also lies within the limits of error of the curve. There is, therefore, no justification, on the basis of the present data, for the application of a correction factor to the high A_K values.

It may be pointed out also that, if the graph of a_{CaO} of Fig.11 is based on the A_R values of the gases, the a_{CaO_R} curve thus obtained will be exactly the same as the a_{CaO_K} curve shown. Therefore, the use of the suffixes K and R when referring to a_{CaO} in CaO-Al_2O_3 slags will be discontinued except when necessary and the curve will be referred to as the a_{CaO} curve. It may also be noted that the a_{CaO_R} points which would have been obtained from runs 26-30 would be slightly higher than the corresponding a_{CaO_K} points (since the ratio A_K/A_R is found to increase with decrease of CO/CO_2 and % SO_2 of the initial gas), but for

these points the increase would be very small. The a_{CaO_R} point corresponding to runs 24 and 25, however, would have been decreased considerably - in fact by the ratio 4.69/7.07, i.e., to 67% of the a_{CaO_K} value or to 58% of the value given by the a_{CaO} v. % CaO curve. It is, therefore, on the basis of this last point that the free energy data of Kelley can be supported in preference to the data of Richardson. It should be noted also, that, in order to make the a_{CaO_R} value of slag A2 fall on the a_{CaO} curve, an experimental result of 1.03%S would have been required, instead of the result of 0.60%S obtained - and such a discrepancy could not be attributed to experimental errors.

The agreement of the results of runs 24-30 with the graph obtained using gases of A_K values of 350 $\pm$ 15 (i.e., runs 7-11, 14-23) is not solely dependent on the accuracy of the free energy data of Kelley. It depends also on the variation of f_{CaS} with sulphur content in any given slag, on the variation of f_{CaS} with slag composition, and on the effect of the absorption of sulphur on the residual N_{CaO} and a_{CaO} values of the slags. In all graphs of results, the values of % CaO and N_{CaO} used were those calculated on the basis of the composition of the slag before any sulphur had been absorbed, and no allowance was made for the effect of sulphur absorption on the value of N_{CaO} and therefore on the "true" a_{CaO} value of a slag of given N_{CaO}. Ideally it would be necessary to equilibrate each slag with a series of gases of progressively decreasing sulphurising potentials, extrapolating to zero sulphur content and thus obtaining the "true" a_{CaO} value of the slag. A limitation is imposed on this method of course, by the difficulty in the analysis of slags of

very low sulphur contents obtained under gases of low sulphurising potentials. The data available from the present series of experiments on $CaO-Al_2O_3$ slags do however indicate certain probable conclusions. Since the results of runs 24-30 lie fairly close to the graph and do not show any trend with either A_K or %S, it can be concluded that the effects of all three factors mentioned above, viz., (1) an error in Kelley's thermodynamic data, requiring a correction to A_K, (2) the variations of %CaS, and (3) the effect of the absorption of sulphur on the residual N_{CaO} value of a slag, and therefore on the "true" a_{CaO} value of the slag, are such as to cancel each other out, or the effect of each factor is within the limits of experimental error. It is probable that the latter is the case since the points on the graph corresponding to runs 24-30 cover the whole range of slag compositions liquid at 1500°C, and do not show any trend with change in A_K or with change in %S in a given slag.

In terms of the ionic model of the constitution of a liquid slag, the above data can be shown to fit into such a picture. When sulphur atoms are introduced into a $CaO-Al_2O_3$ slag the S^{--} ions are held by the Ca^{++} ions less securely than the O^{--} ions which they displace, mainly because of their greater size. The activity of CaO in the melt (in other words, the oxide activity) is not however decreased by an amount corresponding to the S^{--} ion introduced, but by an amount less than this. One would therefore expect that, if a graph of a_{CaO} v. %S were made for any given slag (i.e., of constant initial composition) the a_{CaO} value

would fall slowly from its true value as the sulphur content of the slag increased. From the data at present available, it appears that the variation of a_{CaO} with %S is probably smaller, for the slag sulphur contents used, than the present experimental error limits.

(4) The $CaO-SiO_2$ System.

The results of runs 31-40 are shown in the a_{CaO_K} v. % CaO graph in Fig.13. Since $CaO-SiO_2$ slags at 1500°C are solid between 42.5 and 52% CaO, that portion of the a_{CaO_K} curve in Fig.13 refers to the liquid slag in the supercooled state. Use of the Gibbs-Duhem relation later to determine a_{SiO_2K} helped to establish the shape of the curve. The scatter of points about the a_{CaO_K} curve is rather more than in the case of the $CaO-Al_2O_3$ slags in Fig.11, a fact which may be partly ascribed to the lower sulphur contents of the slags in the $CaO-SiO_2$ runs, and the consequent lower accuracy in their analysis. The a_{CaO_R} curve obtained using the A_R gas values has also been shown in Fig.13 and lies considerably below the a_{CaO_K} curve. The a_{CaO_R} values are all approximately 65% of the a_{CaO_K} values.

The comparison between a_{CaO_K} in $CaO-SiO_2$ and $CaO-Al_2O_3$ slags on a molar basis is shown in Fig.14. It can only be carried out over a very limited range at 1500°C, since N_{CaO} in CaO-rich liquid $CaO-SiO_2$ slags is approximately equal to N_{CaO} in Al_2O_3-rich liquid $CaO-Al_2O_3$ slags. Comparison of the a_{CaO} values at $N_{CaO} = 0.57$ in both systems shows:

$$a_{CaO} \text{ in } 42.2\% \ CaO-Al_2O_3 \text{ slag} = 0.076$$

$$a_{CaO_K} \text{ in } 55.4\% \ CaO-SiO_2 \text{ slag} = 0.033$$

$$a_{CaO_R} \text{ in } 55.4\% \ CaO-SiO_2 \text{ slag} = 0.021$$

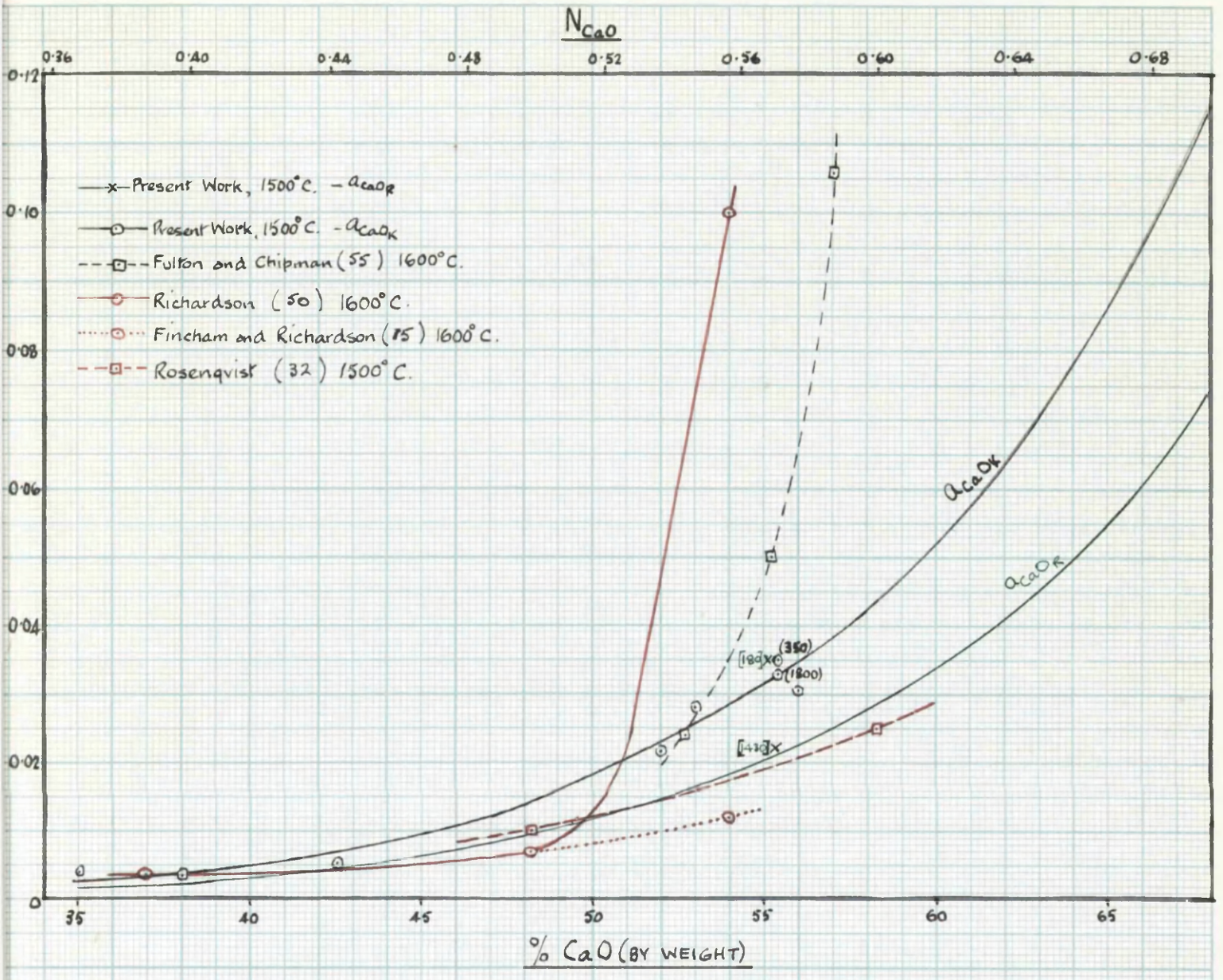


FIG. 13: ACTIVITY OF CaO IN CaO-SiO_2 SLAGS.

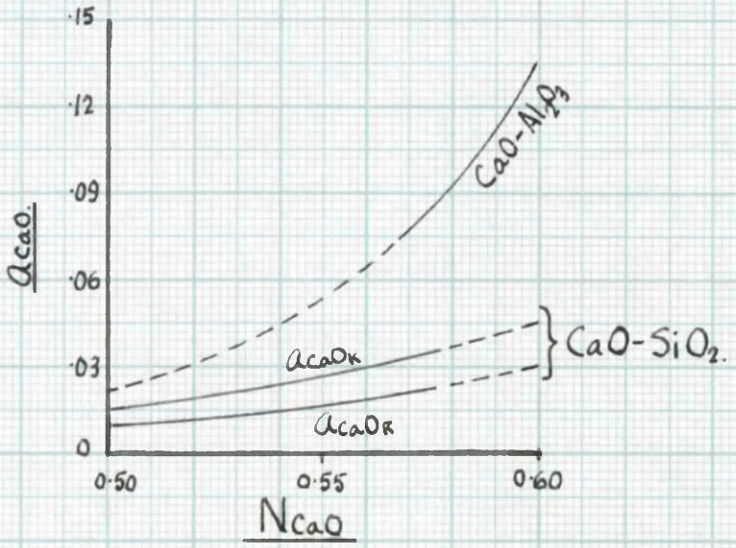


FIG. 14: a_{CaO} IN CaO-Al_2O_3 AND CaO-SiO_2 SLAGS.

i.e., as would be expected from a knowledge of the affinity of CaO for SiO_2 and for Al_2O_3, the activity of CaO in a CaO-SiO_2 slag is much lower than in a CaO-Al_2O_3 slag of the same mole fraction.

(5) The CaO-Al_2O_3-SiO_2 System.

The activities calculated from the experimental data have been used to construct iso-activity curves for a_{CaO_K} in CaO-Al_2O_3-SiO_2 slags at 1500°C, as shown in Figs.15 and 16, in which the activities are plotted against the slag composition expressed in weight % and mole fraction respectively. The corresponding a_{CaO_R} curves have not been calculated. In the low SiO_2 field they do not differ from the a_{CaO_K} curves, since the gases used in the runs in which low-SiO_2 slags were used had A_K values of approximately 350. In the low Al_2O_3 field the a_{CaO_R} values will be approximately 65% of the corresponding a_{CaO_K} values. As can be seen from the diagrams, only a part of the region liquid at 1500°C is covered by the experimental data : the low-SiO_2 field has been fairly well covered, but in the low-Al_2O_3 field only the area with $N_{CaO} > 0.4$ has been investigated.

From Figs.15 and 16, the following points emerge:

(1) Replacement of Al_2O_3 by SiO_2 on a molar basis in the low-SiO_2 field does not materially alter a_{CaO_K}. On a wt. % basis, replacement of Al_2O_3 by SiO_2 results in a slight increase in a_{CaO_K}.

(2) Replacement of SiO_2 by Al_2O_3 on either a molar basis or a wt.% basis in the low-Al_2O_3 field results in a small increase in a_{CaO_K}. Fig.17 illustrates points (1) and (2) in another way, a_{CaO_K} curves for slags of various Al_2O_3/SiO_2 ratios being fairly close to each other in the

FIG. 15: ACTIVITY OF CaO

IN $CaO-Al_2O_3-SiO_2$ SLAGS AT 1500°C.

(COMPOSITIONS EXPRESSED IN WEIGHT %)

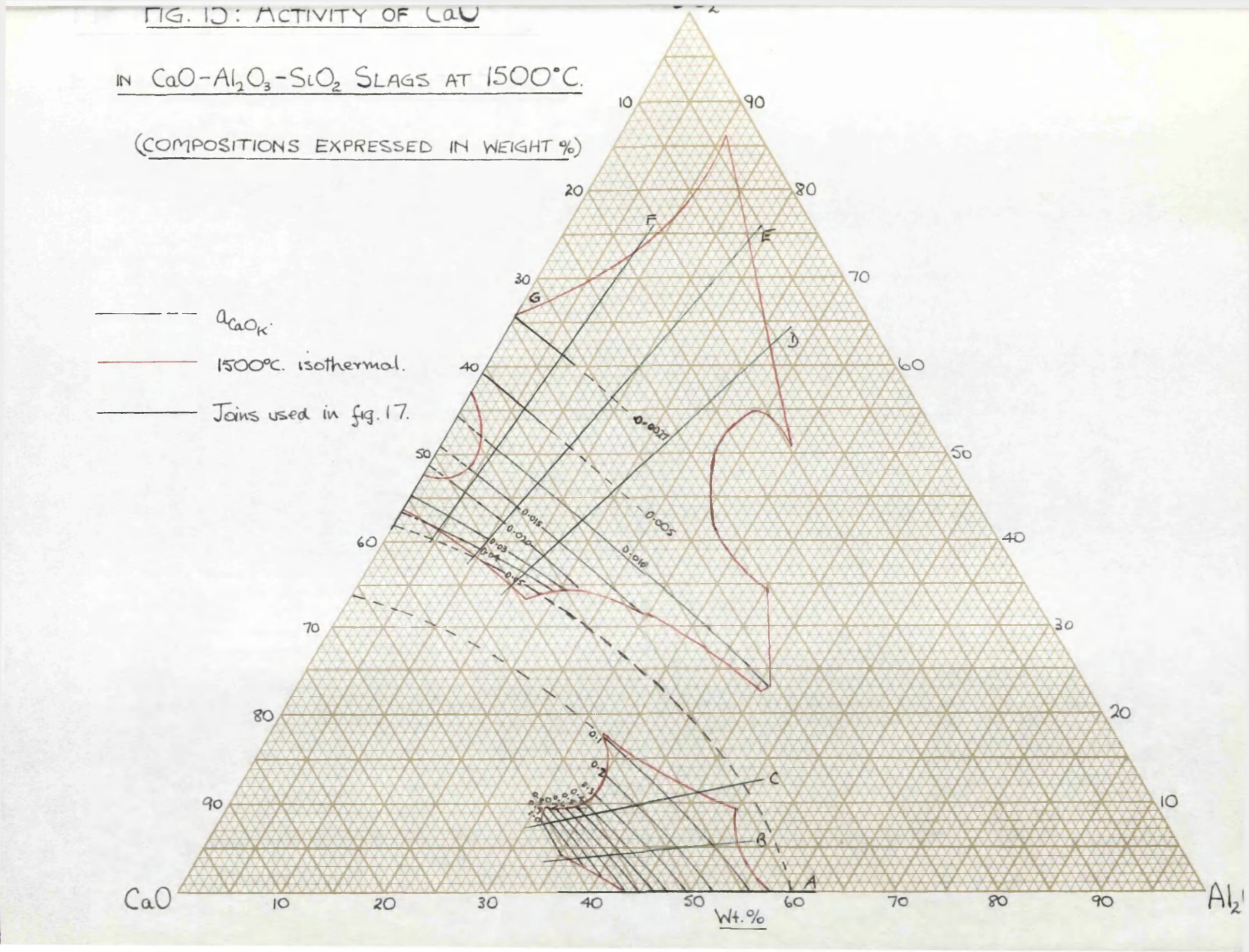
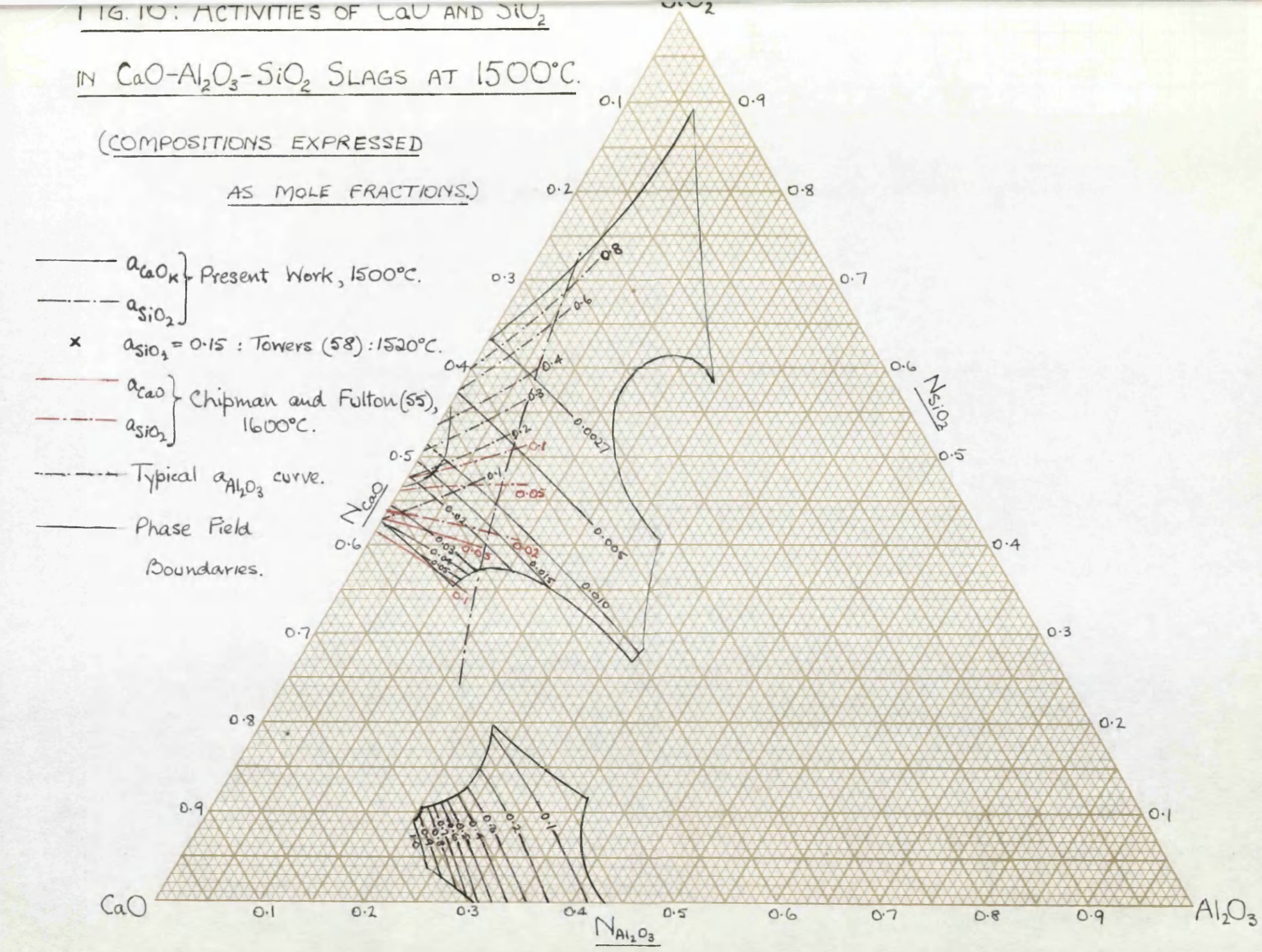


FIG. 10: ACTIVITIES OF CaO AND SiO_2

IN $CaO-Al_2O_3-SiO_2$ SLAGS AT 1500°C.

(COMPOSITIONS EXPRESSED AS MOLE FRACTIONS.)



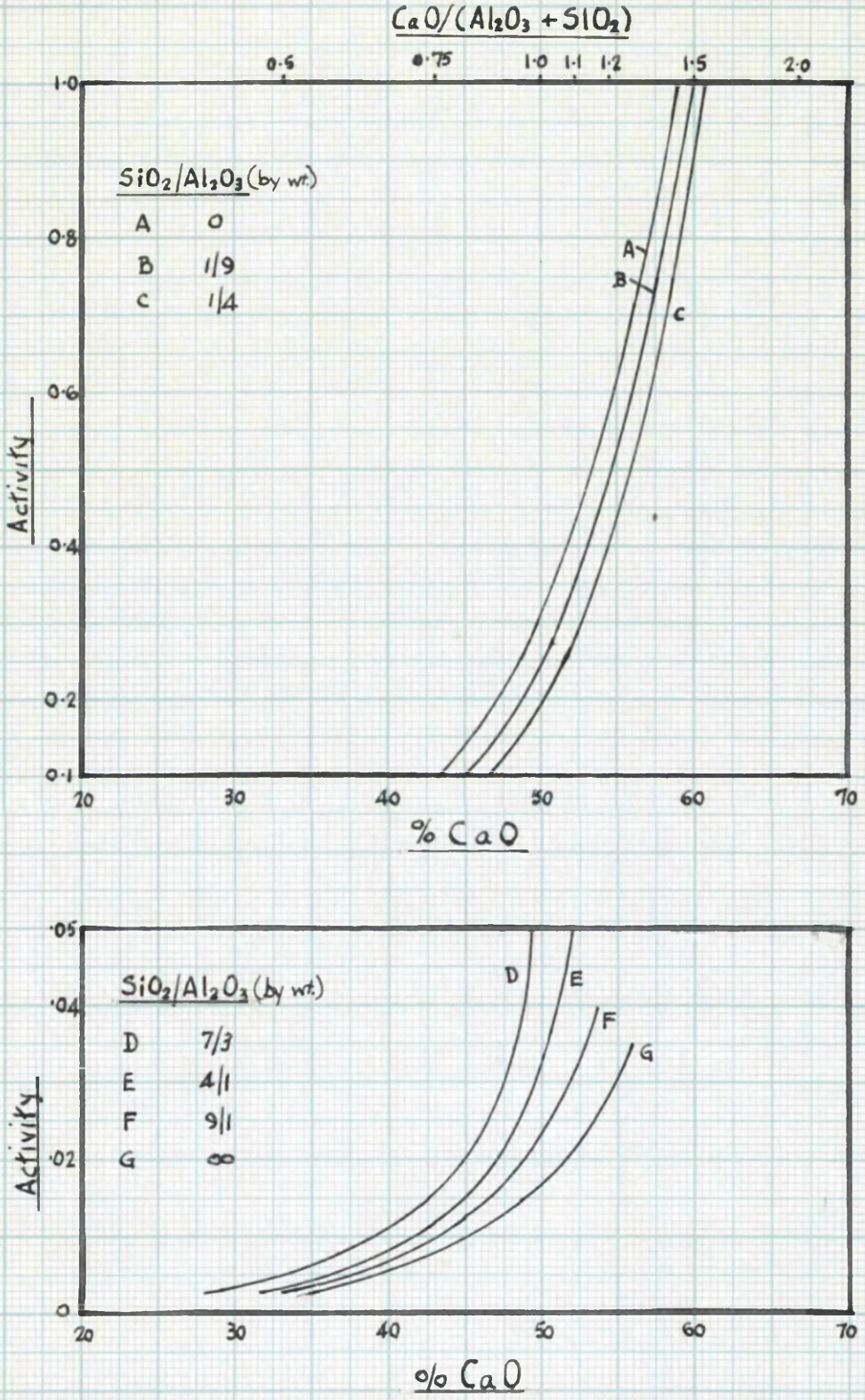


FIG. 17: ACTIVITY OF CaO IN $CaO-Al_2O_3$ SLAGS ALONG STATED JOINS.

case of low-SiO_2 slags. In the case of low-Al_2O_3 slags, the differences between the curves for the various Al_2O_3/SiO_2 ratios are rather greater.

(3) There is a steep drop in a_{CaO_K} with decreasing %CaO along lines of constant Al_2O_3/SiO_2 ratio. This is shown clearly in Fig.17. (The join of constant Al_2O_3/SiO_2 used in this figure are indicated in Fig.15).

(4) The a_{CaO_K} values of slags in the low-SiO_2 field at 1500°C are considerably higher than those in the low-Al_2O_3 field. This is partly due to the higher N_{CaO} values existing in the low-SiO_2 field, but also to the lower affinity of CaO for Al_2O_3 than for SiO_2. The implications of the last two points for iron- and steel-making will be discussed later.

CHAPTER VI.

CALCULATIONS OF THERMODYNAMIC FUNCTIONS AND COMPARISON WITH PREVIOUS DATA.

(1) The $CaO-Al_2O_3$ System.

In order to calculate values of $a_{Al_2O_3}$ from those of a_{CaO} it is necessary to know the value of a_{CaO} in the $CaO-Al_2O_3$ slag which is in equilibrium with solid Al_2O_3. The $CaO-Al_2O_3$ thermal equilibrium diagram (Fig.1), shows that no liquid $CaO-Al_2O_3$ slag is at equilibrium at 1500°C with solid Al_2O_3. It is also very difficult to extrapolate the Al_2O_3 liquidus to 1500°C, since (a) the Al_2O_3 liquidus is not accurately known, and (b) the extrapolation involved is quite a considerable one, since the Al_2O_3 liquidus stops at 1760°C.

The 1500°C isothermal cuts the $CaO.Al_2O_3$ liquidus. Therefore in the first instance, it was decided to calculate values of a_{CaO,Al_2O_3} from the a_{CaO} curve by application of the Gibbs-Duhem relation, and the $a_{CaO.Al_2O_3}$ curve is shown in Fig.11. Although not of great value in itself, this curve, along with the a_{CaO} curve was used to calculate $\Delta\mu_{CaO}$ and $\Delta\mu_{CaO.Al_2O_3}$ curves from which the free energy change for the reaction

$$5CaO_{(s.)} + 7(CaO.Al_2O_3)_{(s.)} = 12CaO.7Al_2O_{3(l)}$$

was calculated to be

$$\Delta G^\circ_{1773} = -39.6 \text{ kcals.}$$

Unfortunately only the most meagre information is as yet available on the free energies of $CaO-Al_2O_3$ melts, and this figure cannot be confirmed at present.

In order to effect a comparison with the free energy given by Fincham and Richardson(15) for $CaO-Al_2O_3$ melts at 1650°C, it was decided to make a tentative extrapolation of the Al_2O_3 liquidus to 1500°C. A figure of 31% CaO was selected as a probable value for the composition

at which the extrapolated Al_2O_3 liquidus would meet the 1500°C isothermal - although the true value may lie anywhere from 27 to 35% CaO. An extrapolation of the a_{CaO} curve to 31% CaO, with the aid of the Gibbs-Duhem $N_{CaO}/N_{Al_2O_3}$ v. log γ_{CaO} graph, gave a value of 0.016 for a_{CaO} at Al_2O_3 saturation. Use of the Gibbs-Duhem relation gave the $a_{Al_2O_3}$ curve shown in Fig.11. The a_{CaO} and $a_{Al_2O_3}$ curves were then used to calculate $\Delta\mu_{CaO}$ and $\Delta\mu_{Al_2O_3}$ curves and the curve of the free energy per mole of reactant for the formation of the melt from solid CaO and solid Al_2O_3 at 1500°C. These curves are shown on the free energy chart, Fig.18. If $a_{Al_2O_3}$ had been taken to be 1 at 35.5% CaO instead of at 31% CaO, the free energy curve would have been raised by 0.5 - 0.8 kcals. Therefore, error limits of $\pm$ 1 kcal may be put on the curve shown in Fig.18.

From this free energy curve, the following free energy change for the reaction

$$12CaO(s) + 7Al_2O_3(s) = 12CaO.7Al_2O_3(l)$$

can be derived:

$$\Delta G^\circ_{1773} = 19 \times (-7.5)$$

$$= -142 \text{ kcals},$$

with an uncertainty of $\pm$ 10kcals.

The free energy curve in Fig.18 gives the value of the free energy change of the reaction producing the liquid slag. Therefore, the point on the curve corresponding to the composition $CaO.Al_2O_3$ represents the free energy, per mole of reactant, of the formation of $CaO.Al_2O_3(l)$, which at 1500°C is in the supercooled state. The free energy of formation of $CaO.Al_2O_3(s)$ however, can be calculated, using the activity product relationship, from the values of a_{CaO} and $a_{Al_2O_3}$ in the slag in equilibrium

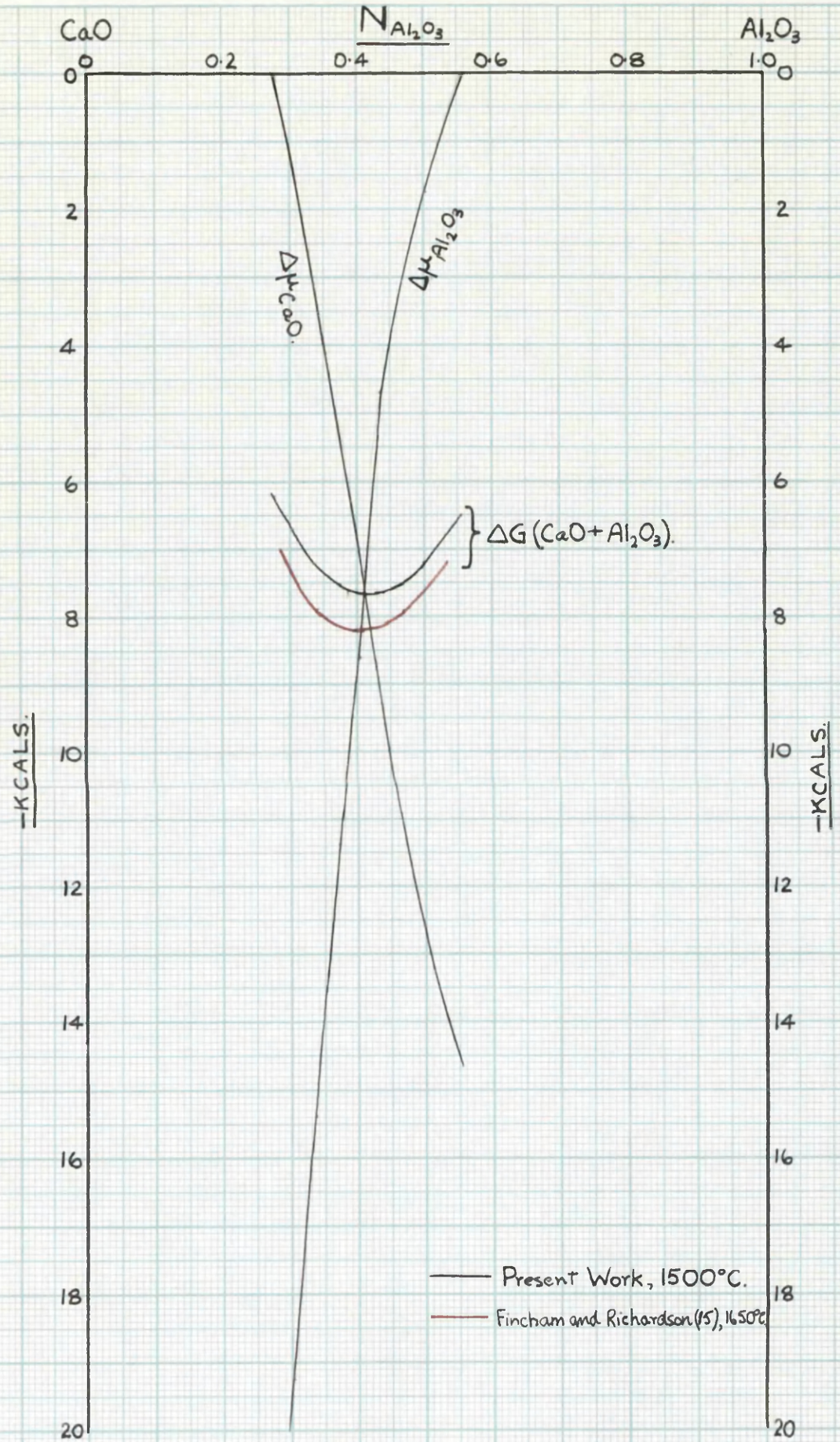


FIG. 18 : THERMODYNAMIC FUNCTIONS OF $CaO-Al_2O_3$ SLAGS.

[RELATIVE TO $CaO_{(s.)}$ AND $Al_2O_{3(s.)}$]

with solid $CaO.Al_2O_3$ at 1500°C. The composition of this slag, from Fig.11, is 42% CaO and for this slag $a_{CaO} = 0.074$ and $a_{Al_2O_3} = 0.20$. For the reaction

$$CaO_{(s)} + Al_2O_{3(s)} = CaO.Al_2O_{3(s)}$$

$$\Delta G^\circ_{1773} = RT \ln a_{CaO}.a_{Al_2O_3}$$

$$= -14.9 \text{ kcals.}$$

The errors involved in this calculation are again relatively large due to the uncertainty of the $a_{Al_2O_3}$ curve. However, if $a_{Al_2O_3}$ had been taken to be 1 at 35% CaO instead of at 31% CaO, the value of $a_{Al_2O_3}$ at 42% CaO would have been 0.33, and the value of $\Delta G^\circ_{CaO.Al_2O_3}$ at 1500°C -13.1 kcals. Even if $a_{Al_2O_3}$ had been 0.5, $\Delta G^\circ_{CaO.Al_2O_3}$ at 1500°C would then have been -11.6 kcals. Hence error limits of ±3 kcals may be assigned to the value of -14.9 kcals. given above. This value is also reasonable when compared with the value of -19.5 kcals. obtained for the corresponding silicate, $CaO.SiO_2$ (see later), which would be expected to be larger numerically from a consideration of the relative affinities of CaO for Al_2O_3 and for SiO_2.

The only comparable data on a_{CaO} in $CaO-Al_2O_3$ melts are those given by Fincham and Richardson(15). Most of their work on $CaO-Al_2O_3$ melts was carried out at 1650°C but from the approximate CaS saturation limit in a 52.4% CaO slag at 1500°C, they calculate $a_{CaO} = 0.5$. This value has been plotted on Fig.11 and agrees very well with the present work, being only 12% higher than the a_{CaO} curve of the present work.

Three values of a_{CaO}, obtained by Fincham and Richardson(15) at 1650°C assuming $\gamma_{CaS} = 5$, have also been plotted in Fig.11. Since

at 1650°C, $a_{CaO} = 1$ at 62% CaO, this point has also been plotted in Fig.11 and a smooth curve drawn through it and the afore-mentioned three points. This curve lies considerably below that obtained from the present work at 1500°C, except at low N_{CaO} values. This must, of course, be true for the high CaO compositions, but whether the two a_{CaO} curves cross at lower N_{CaO} curves depends largely on the shape of the $\Delta H(CaO+Al_2O_3)$ curve. Unfortunately the latter is not known. It would be expected, however, to be similar in form to that for $CaO \cdot SiO_2$ melts given by Richardson(51), shown in Fig.20, which indicates that a_{CaO}(1600°C) should exceed a_{CaO}(1500°C) when N_{CaO} falls below 0.47. Fig.11 shows that the curves cross at approximately $N_{CaO} = 0.52$. Although this figure is not in disagreement with the corresponding value for the $CaO-SiO_2$ system, it is, however, felt that the value of 5 for γ_{CaS} assumed by Fincham and Richardson(15) in calculating their a_{CaO} values is low and that their a_{CaO} curve for 1650°C should lie higher than is indicated by them. The curves would then cross at a somewhat higher N_{CaO} value (~ 0.6). The assumed value of 5 corresponds to a solubility of sulphur of 8.6% S at 1650°C in a $CaO-Al_2O_3$ slag of $N_{CaO}/N_{Al_2O_3} = 2.0$. However, it can be calculated from their data that the solubility of sulphur in the same slag at 1500°C is approximately 4.1% and that γ_{CaS} is 10.7 at this temperature. Whereas the solubility of sulphur would be expected to increase with rise in temperature, a more than twofold increase seems unusually large.

It seems desirable at this point to examine the assumptions made in the present work regarding the constancy of γ_{CaS} (a) in a given slag

over the range of sulphur contents used, and (b) in $CaO-Al_2O_3-SiO_2$ slags of the range of compositions used in the present work, as far as the available data allow, and to compare the values of γ_{CaS} given by the present work with the values used by other workers.

(a) In the calculation of a_{CaO}, the assumption was made that a_{CaS} is proportional to weight %S up to 2%. In the light of the discussion on pp. 72-74, the available data can be used to show to what extent this assumption is true over the range of sulphur contents used. For the reaction:

$$CaO + \tfrac{1}{2}S_2 = CaS + \tfrac{1}{2}O_2$$

$$K = \frac{a_{CaS}}{a_{CaO}} \cdot \frac{(P_{O_2})^{\frac{1}{2}}}{(P_{S_2})^{\frac{1}{2}}} = \frac{\gamma_{CaS} \cdot N_{CaS}}{a_{CaO} \cdot A_K}$$

Considering slag AS1 and the results of runs 23 and 30, and assuming that $a_{CaO} = 1.00$ in both slags as they exist at equilibrium with the gases concerned, i.e., that the partial replacement of O by S does not significantly lower the a_{CaO} value, then:

for run 23: $A_K = 340$, $a_{CaO} = 1$, %S in slag = 1.79, $\therefore N_{CaS} = 0.0374$

$$\therefore \gamma_{CaS} = \frac{1 \times 340 \times K}{0.0374} = 9090K$$

for run 30: $A_K = 168$, $a_{CaO} = 1$, %S in slag = 0.88, $\therefore N_{CaS} = 0.0182$

$$\therefore \gamma_{CaS} = \frac{1 \times 168 \times K}{0.0182} = 9230K$$

$$\therefore \gamma_{CaS} \text{ (at 1.79\%S)} / \gamma_{CaS} \text{(at 0.88\%S)} = 0.985$$

Therefore, within the limits of experimental error, and assuming that variables (1) and (3) on p.73 have no appreciable effect, the above shows that γ_{CaS} in slag AS1 is constant for slags containing up to 1.8%S. This agrees with the work of Fincham and Richardson(15) which shows

(see p20) that γ_{CaS} at 1500°C is constant up to at least 1.3%S.

(b) The question of whether γ_{CaS} in $CaO-Al_2O_3-SiO_2$ slags at 1500°C is substantially constant (as has been assumed in the present work) is a difficult one to answer. Deductions from the present work and the data given by previous workers can however be compared here.

The sulphur content of slag AS1 at which saturation occurs can be estimated approximately from certain experimental data obtained in the present work. A preliminary experiment using slag A10 gave sulphur contents of 4.5 and 6.1% (see run 88 in Table IV) but the bulbous appearance of the slag suggested that the sulphur saturation content had been exceeded. Later, calculations based on the mean S/A_K value of slag A10 indicated that a value of 2.9% sulphur should have been obtained in run 88. Therefore, it is concluded that saturation of slag A10 occurs at less than 2.9% S and at greater than 0.46% S - the experimentally obtained figure which gave a satisfactory result (run 29). In addition a run using slag AS6 gave an equilibrium sulphur content of 2.52% S (see run 89, Table VI). This slag was minutely crystalline in appearance, like many others, and did not appear to be above the sulphur saturation content. The result of 2.52%S has not, however, been used since it exceeds the limit of 2% S above which it had been decided to reject results. The a_{CaO} value obtained for slag AS6 using this result is in fact about 11% higher than that obtained from the equilibrium sulphur content of run 46 of 0.46%S. γ_{CaS} at 2.5% S would be expected to be less than γ_{CaS} at 0.46%S. If allowance had been made for the lower value of γ_{CaS} in the slag of 2.52%S, the a_{CaO} value thus obtained would

have agreed more closely with the a_{CaO} value obtained from run 46. The results of these two runs can be used as pointers to the sulphur saturation value of slag AS1. The saturation value of $CaO-Al_2O_3-SiO_2$ slags with CaS would not be expected to vary greatly for slags of the same basicity. From Table IV, it can be seen that the N_{CaO} value of the standard slag AS1 does not greatly exceed the N_{CaO} value of slags S10 and AS6. Therefore, an approximate estimate of the sulphur content at saturation of slag AS1 is 3.0% S, and it is improbable that this figure should be lower than 2.5% S or greater than 4%S. The corresponding values of γ_{CaS} are:

if saturation in slag AS1 occurs at 3.0% S, $\gamma_{CaS} = 16$,

at 2.5% S, $\gamma_{CaS} = 19$,

and at 4.0% S, $\gamma_{CaS} = 12$.

These γ_{CaS} figures are rather higher than the figure deduced from the work of Fincham and Richardson(15) of $\gamma_{CaS} = 10.7$ in a $CaO-Al_2O_3$ slag of $CaO/Al_2O_3 = 2.00$ at 1500°C. The solubility figures deduced from the present work are rather lower than most of the data obtained by other workers for various $CaO-Al_2O_3-SiO_2$ slags and given in Chapter III (p.18), figures of from 4 to 11% S being given by these workers. There is, therefore, no more than an approximate agreement between all the data available, but it is rather difficult to come to any definite conclusions. It does appear, however, that the value of $\gamma_{CaS} = 5$, assumed by Fincham and Richardson is rather low, and that a value of 10-15 at 1500°C in the slags used in the present work is more likely. It also appears likely that there is some variation in the value of γ_{CaS} with slag

composition, and although the extent of this variation in the value of γ_{CaS} with slag composition cannot be determined, γ_{CaS} will probably vary within such limits as 12 ± 5. It is therefore highly desirable that more accurate data be obtained on the variations of γ_{CaS} and on the solubility of CaS in slags. As far as the present work is concerned the results can only be presented by assuming γ_{CaS} is constant and the possibility of errors arising from this assumption is noted for future correction.

Further deductions can be made from the data on the standard slag. It has been shown that

$$K = \frac{a_{CaS}}{a_{CaO}.A}$$

For the standard slag, $a_{CaO} = 1$, and when saturated with S, $a_{CaS} = 1$.
Under these conditions, $K.A = 1$

Using the A_K gas values and assuming saturation of slag AS1 with sulphur is at 3.0% S, then, since S/A_K for slag AS1 is 52.7×10^{-6}, it can be shown that the A_K value of the gas required to obtain an absorption of 3.0% S is 569.

$$\therefore K_{1773} = 1.76 \times 10^{-3}$$

Therefore for the reaction $CaO_{(s)} + \frac{1}{2}S_2 = CaS_{(s)} + \frac{1}{2}O_2$

$$\Delta G^{\circ}_{1773} = +22.4 \text{ kcals.}$$

If saturation were at 2.5% or 4.0% S, this figure would be +21.7 or +23.4 kcals. respectively. However, if the A_R gas values had been used, the free energy for the reaction would have been +20 kcals. It has been shown (p.65) that the free energy equation deduced from the work of Rosenqvist(32) and Richardson and Jeffes(34)(36) is

$$\Delta G^{\circ}_{T} = +21,770 - 0.7T$$

$$\therefore \Delta G^{\circ}_{1773} = +20.5 \text{ kcals.}$$

Although Rosenqvist's free energy data appear to support the choice of the A_R gas values, his work was carried out at temperatures not exceeding 1425°C., and it did not take into consideration the possibility of compounds such as HS or SO being formed. It is difficult to assess how these factors would affect the free energy equation obtained, but they may account for the difference between the value for the free energy of the reaction at 1500°C, deduced from Rosenqvist's work and the value obtained using the A_K gas values in the present work. In view of the discussion in the previous Chapter in support of the A_K values , it is felt that Rosenqvist's work is not strongly enough evidenced to warrant any changes in the conclusions given there, i.e., that the A_K values are to be preferred to the A_R values. On the other hand, the conclusions of the present work themselves require further evidence and it is therefore desirable to show the results based on the A_R values where these results differ significantly from those obtained using the A_K values.

Comparison can be made between the free energy curves for CaO-Al_2O_3 slags obtained at 1500°C from the present data and at 1650°C from the work of Richardson and Fincham(15). If it is assumed that the values of $\Delta H(CaO + Al_2O_3)$ are of the same order as the values of $\Delta H(CaO + SiO_2)$ given in Fig.20, then the difference between the free energy curves due to the effect of the 150°C difference in temperature is approximately 200-400 cals., which means that there is a remarkably close agreement between the two curves. It must be pointed out that, in view of the

assumptions made in obtaining each curve, the close agreement between the two curves cannot be taken as a guarantee of a high degree of accuracy but only as confirmation that the free energy curve given by Fincham and Richardson is correct to within the probable uncertainty figure of ± 2 kcals. given by them.

(2) The $CaO-SiO_2$ System.

By the application of the Gibbs Duhem relation, values of a_{SiO_2} were calculated from the a_{CaO_K} curve and are shown in Fig.19. Since the values of a_{CaO_R} are an approximately constant proportion of the values of a_{CaO_K}, the N_{CaO}/N_{SiO_2} v. $\log \gamma_{CaO}$ Gibbs-Duhem graph obtained from the a_{CaO_R} curve is the same as that obtained from the a_{CaO_K} values, differing only in its position relative to the $\log \gamma_{CaO}$ axis. Consequently the a_{SiO_R} durve coincides with the $a_{SiO_{2K}}$ curve. Therefore, the use of the suffixes K and R with a_{SiO_2} will be discontinued. The a_{CaO_K} and a_{SiO_2}, and the a_{CaO_R} and a_{SiO_2} curves were then used to calculate curves of $\Delta\mu_{CaO_K}$, $\Delta\mu_{CaO_R}$, $\Delta\mu_{SiO_2}$ and curves for the free energy of formation per mole of reactant of the melt from solid CaO and solid SiO_2, denoted by ΔG_K and ΔG_R respectively. These curves have been plotted on the free energy chart, Fig.21. As would be expected, the ΔG_R curve is similar in shape to the ΔG_K curve but slightly lower than it, the difference being from 0.5 to 1.0 kcals. For the purposes of comparison with the free energy curves obtained by other workers, it was desirable to determine the position of the minimum of the curves obtained in the present work. Therefore, the a_{CaO_K} and a_{CaO_R} curves were extra-

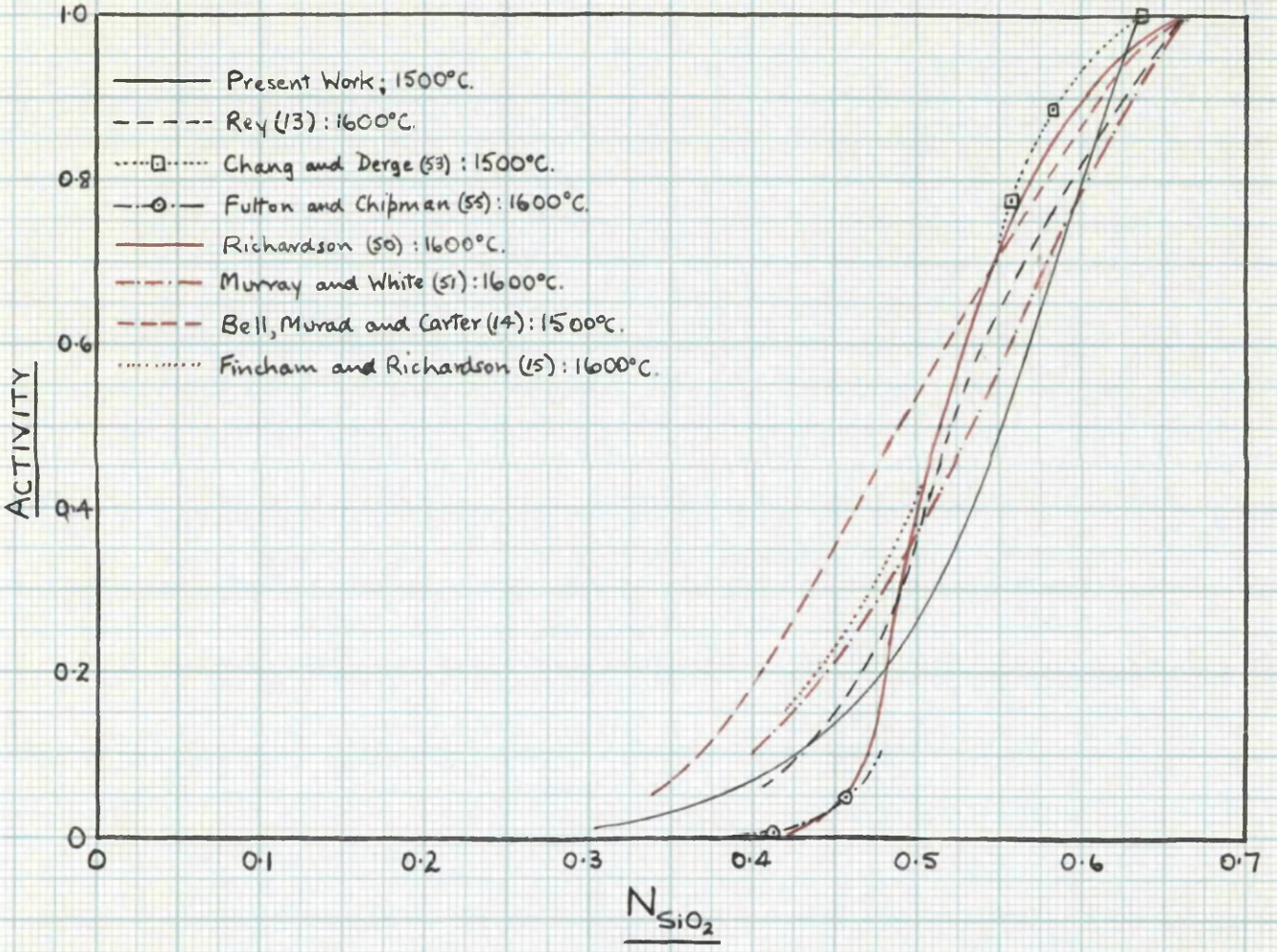


FIG. 19 : ACTIVITY OF SiO_2 IN $CaO-SiO_2$ SLAGS.

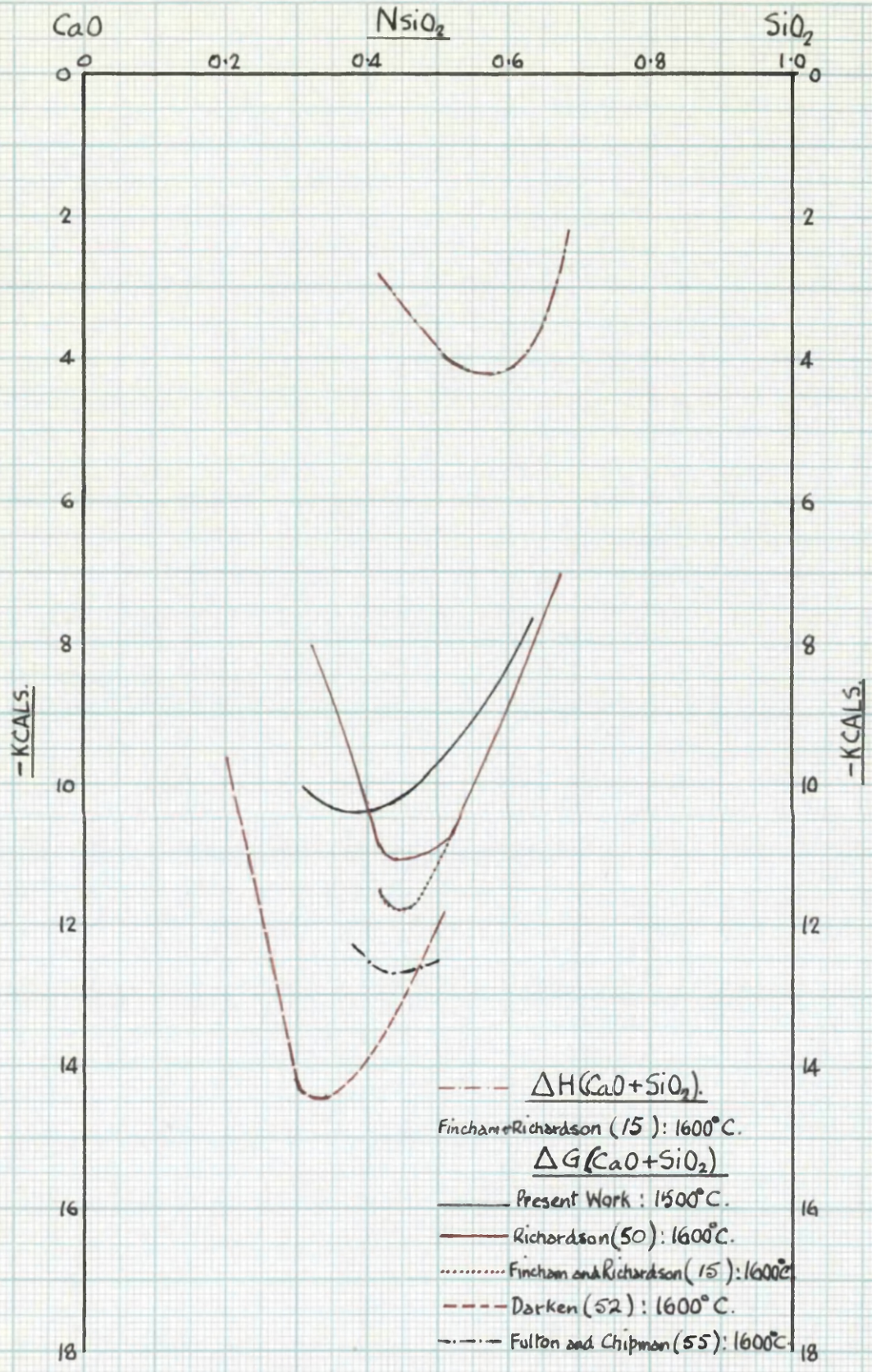


FIG. 20: THERMODYNAMIC FUNCTIONS OF $CaO-SiO_2$ SLAGS.

[RELATIVE TO $CaO_{(s)}$ AND $SiO_{2(s)}$]

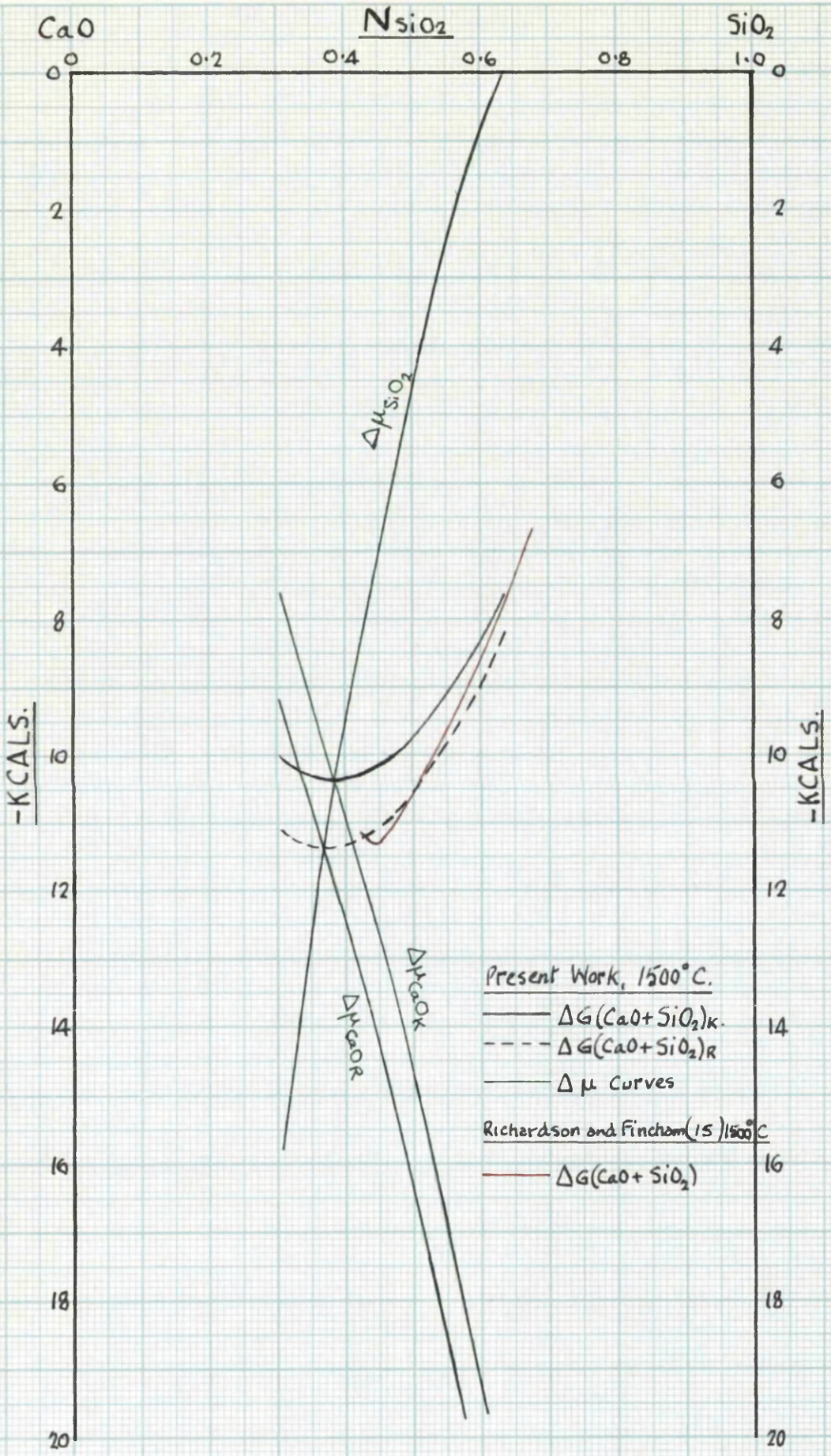


FIG. 21: THERMODYNAMIC FUNCTIONS OF $CaO-SiO_2$ SLAGS AT 1500°C.
[RELATIVE TO $CaO_{(s)}$ AND $SiO_{2(s)}$]

polated to 68% CaO with the aid of the N_{CaO}/N_{SiO_2} v. log γ_{CaO} graph used in the calculation of a_{SiO_2} by the Gibbs-Duhem relation, and the corresponding a_{SiO_2} values calculated. The free energy curves derived from these values showed minimum values as follows:

$\Delta G(CaO+SiO_2)_K$ curve - minimum value = -10.4 kcals. at N_{SiO_2} = 0.38

$\Delta G(CaO+SiO_2)_R$ curve - minimum value = -11.4 kcals. at N_{SiO_2} = 0.37

The free energy curves also indicate the following values for the free energy of formation of the compound $CaO.SiO_2$ at 1500°C

$$CaO(s) + SiO_2(s) = CaO.SiO_2(l)$$

$$\Delta G^\circ_{1773}(K) = -19.5 \text{ kcals.}$$

$$\Delta G^\circ_{1773}(R) = -21.1 \text{ kcals.}$$

Since $CaO.SiO_2$ does not melt till 1540°C it will be noted that this free energy equation refers to $CaO.SiO_2$ in the supercooled liquid state.

The free energy of formation of the compound $2CaO.SiO_2$ was calculated from the activity product relationship,

$$\Delta G^\circ_{1773} = -RT \ln a^2_{CaO} \cdot a_{SiO_2}$$

where a_{CaO} and a_{SiO_2} refer to the activities of CaO and SiO_2 in the liquid $CaO-SiO_2$ slag in equilibrium with solid $2CaO.SiO_2$ at 1500°C. The values obtained were as follows:

$$2CaO(s) + SiO_2(s) = 2CaO.SiO_2(s)$$

$$\Delta G^\circ_{1773}(K) = -31.9 \text{ kcals.}$$

$$\Delta G^\circ_{1773}(R) = -35.0 \text{ kcals.}$$

The results of the present work may be compared with the limited amount of experimentally determined free energy and activity data for the $CaO-SiO_2$ system which has so far been published, and also with theoretical comput-

•ations made recently by Richardson(50), Rey(13), Murray and White(51) and Darken(52). Chang and Derge(53) gave 2 values for a_{SiO_2} at 1500°C and these are indicated in Fig.19. The agreement with the present work is not good. Further comment on Chang and Derge's results will be made when considering their a_{SiO_2} values in $CaO-Al_2O_3-SiO_2$ slags.

Richardson and co-workers have given data on the $CaO-SiO_2$ system in various papers. In their collection of data on compounds of interest in iron and steel-making, Richardson, Jeffes and Withers(54) summarised the available data on the compounds $CaO.SiO_2$, $2CaO.SiO_2$ and $3CaO.SiO_2$. From this data, Richardson(50) deduced the free energy curve for $CaO-SiO_2$ slags at 1600°C., which is shown in Fig.20. As a result of the experi•mental work of Fincham and Richardson(15), this curve was amended over the range $N_{SiO_2} = 0.4 - 0.5$ and the amended portion of the curve is also shown in Fig.20. The values of a_{CaO} at 1600°C obtained from the curve of Richardson(50) and the value used by Fincham and Richardson(15) to amend the free energy curve have been plotted in Fig.13. The corres•ponding values of a_{SiO_2} have been plotted in Fig.19.

A fair comparison between the results of the present work and those of Fincham and Richardson(15) must make allowance for two factors:

(1) the work of Fincham and Richardson was carried out at 1600°C while the present work was carried out at 1500°C., and

(2) the work of Fincham and Richardson is based on the thermodynamic data given by Richardson et al(36), whereas the evidence of the present work favours the data put forward by Kelley(35).

To eliminate the differences due to (2), the a_{CaO_R} and $\Delta G(CaO+SiO_2)_R$ data obtained in the present work must be used, and not the data based on the A_K gas values. It is also possible to eliminate the effect of the difference in temperature in the following way. Fincham and Richardson(15) in addition to giving the $\Delta G(CaO+SiO_2)_{1873}$ curve, also gave the $\Delta H(CaO+SiO_2)_{1873}$ curve (shown in Fig.20). The $\Delta H(CaO+SiO_2)_{1873}$ curve can be assumed to hold for 1500°C also since the difference due to 100°C change in temperature is negligible. Therefore, from the ΔH_{1873} and ΔG_{1873} curves given by Fincham and Richardson, the ΔG_{1773} curve was calculated and is shown in Fig.21. However, it is much more accurate to derive a ΔG curve from activity values than to derive activities from the intercepts of the tangents to the ΔG curve. Comparison between the present work and the work of Fincham and Richardson is therefore best made between the ΔG_{1773_R} curve and the ΔG_{1773} curve deduced from the work of Fincham and Richardson. From Fig.21, it can be seen that the two curves are substantially in agreement. Therefore, the differences between the a_{CaO_R} curve and the a_{CaO} curve of Fincham and Richardson seen in Fig.13, are to be attributed mainly to the difference in temperature. The only real points of disagreement between the two free energy curves are in the position of the minimum and in the shape of the curve at N_{SiO_2} values less than about 0.50. In the case of the present work, the shape of this portion of the curve depends on experimental results from N_{SiO_2} = 0.5 - 0.42, and on the extrapolation of the a_{CaO_R} curve at N_{SiO_2} values below 0.42, whereas in the case of the ΔG_{1773} curve deduced from the work of Fincham and Richardson, the portion of this curve corresponding to N_{SiO_2} values

less than about 0.5 depends on two data for the support of which adequate evidence is not available. These two data are:

(1) the a_{CaO} value given by Fincham and Richardson for N_{SiO_2} = 0.44 [which in turn is derived, very indirectly, from their results by assuming that γ_{CaS} has an approximately constant value of 5 over the range of $CaO-SiO_2$ slags used in their work (i.e., N_{CaO} = 0.39-0.56)]. Fincham and Richardson did show that this value has some support but at best it can only be very approximate.

(2) the assumption that the ΔG_{1873} curve at N_{SiO_2} values less than 0.44 is approximately parallel to the ΔG_{1873} curve given by Richardson(50) which itself depends only on one point of rather doubtful accuracy at N_{SiO_2} = 0.33.

Since the results of the present work are based on experimental work, in which a fair number of precautions have been taken to ensure the accuracy of the results obtained, it is thought that the portion of the $\Delta G(CaO+SiO_2)_{1773R}$ curve at N_{SiO_2} values less than about 0.5, is more accurate than the corresponding portion of the $\Delta G(CaO+SiO_2)_{1773}$ curve given by Fincham and Richardson. It should also be noted, that although Fincham and Richardson do not state the probable uncertainty to be ascribed to their $\Delta G(CaO+SiO_2)$ curve, examination of the data used in compiling it indicate that it is at least $\pm$ 1 kcal., and this uncertainty is sufficiently great to enable it to be said that the $\Delta G(CaO+SiO_2)$ curve given by Fincham agrees with both the $\Delta G(CaO+SiO_2)_K$ curve and the $\Delta G(CaO+SiO_2)_R$ curve obtained in the present work.

Fulton and Chipman(55) have lately deduced values of a_{SiO_2} at 1600°C from their experiments on the reduction of SiO_2 from $CaO-Al_2O_3-SiO_2$

slags by carbon-saturated iron. Their values of a_{SiO_2} in $CaO-SiO_2$ slags are shown in Fig.19, and agree remarkably well, as they stated, with the a_{SiO_2} values derived by Richardson(50). Fulton and Chipman's values of a_{SiO_2} in $CaO-SiO_2$ slags do not agree so closely with the a_{SiO_2} values derived from the amended free energy curve of Fincham and Richardson, as can be seen from Fig.19. Fulton and Chipman's curve is also considerably below the a_{SiO_2} (1500°C) curve derived from the present work. Unfortunately their work covers only part of the range of slag composition covered by the present work. The agreement of the present work with the various other a_{SiO_2} curves shown in Fig.19 is also better than that of Fulton and Chipman's curve with them. A possible reason for this is that the work of the latter authors is based on the thermodynamic data of γ_{Si}^{C} in Fe-Si-C melts which is regarded as being, as yet, not too reliable.

Fulton and Chipman calculated values of a_{CaO}(1600°C) from their a_{SiO_2} curve using the Gibbs-Duhem relation and the activity product relationship $K = a^2_{CaO} \cdot a_{SiO_2}$ where K is derived from the free energy of formation of $2CaO.SiO_2$. The free energy equation which they used is as follows:

$$2CaO(s) + SiO_2(s) = 2CaO.SiO_2(s)$$

$$\Delta G^{\circ}_T = -26,200 - 4.9T$$

$$\Delta G^{\circ}_{1873} = -35.4 \text{ kcals.}$$

Their a_{CaO}(1600°C) curve is shown in Fig.13, and as would be expected, is considerably higher than the a_{CaO} curves obtained in the present work. The a_{CaO} and a_{SiO_2} curves obtained by Fulton and Chipman were used to calculate the $\Delta G(CaO+SiO_2)_{1873}$ curve shown in Fig.20. It is interesting

to note that Fulton and Chipman's $\Delta G(CaO+SiO_2)_{1873}$ curve does not show the agreement which might be expected, on the grounds of the agreement of the a_{SiO_2} curves, with the $\Delta G(CaO+SiO_2)_{1873}$ curves given by Richardson(50). This is due to the difference between the values of the free energy of formation of $2CaO.SiO_2$ used in the two sets of data - the value used by Richardson being -30 kcals., and that used by Fulton and Chipman -35.4 kcals.

Fulton and Chipman's free energy curve agrees, within the limits of uncertainty, with both the free energy curves obtained in the present work, i.e., ΔG_R and ΔG_K, the difference between it and the ΔG_R curve being 1 kcal., and between it and the ΔG_K curve being 2 kcals. However, on account of the assumptions involved in calculating the a_{CaO} and ΔG_{1873} curves from Fulton and Chipman's experimental data, the conclusion that Fulton and Chipman's work favours the choice of the ΔG_R curve rather than the ΔG_K curve is not justified.

Rey(13) deduced silica activities in $CaO-SiO_2$ melts at 1600°C from liquid immiscibility and melting point diagrams, his a_{SiO_2} curves being shown in Fig.19. He admits, however, that the graph is only approximate, firstly because of the assumption made in the derivation of the equation used to compute the activity of a component, viz., that the solution was "regular", and secondly, because this equation can only be used when the slag composition is such that the solid deposited when the liquidus is reached is the pure component, in this case cristobalite, i.e., the equation can only be used from 68-64.5% SiO_2 at 1600°C. Below 64.5% SiO_2, the trend of the a_{SiO_2} curve was obtained by Rey, through the approximate similarity between the slope of the activity curve and that of

the solidification curve and through a_{SiO_2} being small when compositions are reached at which stable silicates are formed. At 1500°C, the range of compositions over which values of a_{SiO_2} can be calculated is 65 - 64.5% SiO_2, and over this very small range (where a_{SiO_2} = 1 - 0.98) it is not surprising that the graph obtained duplicates the results of the present work. The trend of the a_{SiO_2} graph at 1600°C given by Rey is probably consistent with that of the present work at 1500°C., but it is obvious that this method is not suitable for confirming the results of the present work.

Murray and White(51) deduced a_{CaO} and a_{SiO_2} at 1600°C from the dissociation constants of $CaO.SiO_2$ and $2CaO.SiO_2$. They stressed that this treatment was "purely formal" and in no way inferred the existence of molecular entities in the slag, nor was it a solution of the problem of slag constitution. Their values are referred to liquid silica as the standard state and if divided by 0.509 (the factor between the activities referred to liquid and solid silica), can be compared with the present work. Their graph is shown on Fig.19. (It may be noted that it very nearly coincides with the curve of Chang and Derge(53) for a_{SiO_2} at 1600°C). However, it cannot be used for more than a general comparison with the present work.

Darken(52) has given a semi-quantitative free energy curve for the $CaO-SiO_2$ system at 1600°C, which he has constructed by using the free energy data of Chipman and co-workers and by calculating the free energies by a method recently devised by himself. The curve is shown in Fig.20 and is rather lower than the curves obtained in the present work and

than that given by Richardson(50) and corrected by Fincham and Richardson (15). Rosenqvist(32) used Darken's chart to deduce two values of a_{CaO} at 1500°C and these values are indicated in Fig.13. They agree very well with the a_{CaO_R} curve obtained in the present work. However, Rosenqvist has stated that these values are only approximate, and they cannot therefore be used to support the a_{CaO_R} curve rather than the a_{CaO_K} curve. Bell, Murad and Carter(14), assumed values for a_{CaO} of 1 at $N_{SiO_2} = 0$ almost to $a_{CaO} = 0$ at $N_{SiO_2} = 0.33$, and, with Rosenqvist's values at less basic compositions, used the Gibbs-Duhem relation to calculate the a_{SiO_2} curve which is shown in Fig.19. The assumptions involved make this a very arbitrary graph and no useful comparison can be made with the present work.

A summary of the data available on the $CaO-SiO_2$ system can now be given. A comparison of all the a_{CaO} curves given in Fig.13, shows that, apart from the curves given by Fulton and Chipman(55) and by Richardson(50). there is a fair measure of agreement.

A comparison of all the a_{SiO_2} curves given in Fig.19 shows that the curve derived from the present work agrees fairly well with most of the other curves given. The present work is based more on direct experimental data than any of the other curves, excepting possibly that of Fulton and Chipman(55). Therefore, and because of the other reasons given above, it is felt that it is more accurate than the other activity curves given.

From a comparison of the free energy curves given in Figs.20 and 21, it can be seen that there is a general measure of agreement between

the curves obtained from the present work and most of the other curves given. The semi-quantitative curve given by Darken(52) is the only one which is outwith the probable errors involved in the derivation of the curve based on the present work. The agreement with the curve given by Fincham and Richardson(15) especially is very good. The shape of the curves based on the present work at N_{SiO_2} values less than 0.5 is flatter than that of any of the other curves given. The present curve is regarded as being more accurate, since the free energies of formation (per mole of reactant) of the two compounds $CaO.SiO_2$ and $2CaO.SiO_2$ are approximately the same, and therefore, for melts with compositions between those of these two compounds, very little difference might be expected in the free energy of formation of the melt over that range of N_{SiO_2} values.

The values given by the various workers for the free energies of formation of the two compounds may also be compared as follows. For the reaction

$$CaO_{(s)} + SiO_{2(s)} = CaO.SiO_{2(s)}$$

Richardson, Jeffes and Withers(54) give

$$\Delta G^{\circ}_{1773} = -2.4 \text{ kcals.}$$

the error limit assigned to this value being $\pm$ 3kcals. The values given by other workers are for the reaction

$$CaO_{(s)} + SiO_{2(s)} = CaO.SiO_{2(l)}$$

Fincham and Richardson(15) give

$$\Delta G^{\circ}_{1873} = -22 \text{ kcals.}$$

By extrapolation of the free energy curve obtained from the data of Fulton and Chipman(55), the following value is obtained

$$\Delta G^{\circ}_{1873} = -24.5 \text{ kcals.}$$

Darken(52) gives

$$\Delta G^{\circ}_{1873} = -24 \text{ kcals.}$$

The values obtained in the present work are at 1500°C., but from the $\Delta H(CaO+SiO_2)_{1873}$ curve given by Fincham and Richardson(15), the difference due to the 100°C difference in temperature has been shown to be ~400 cals. and can therefore be neglected. These values are

$$\Delta G^{\circ}_{K} = -19.5 \text{ kcals., and}$$

$$\Delta G^{\circ}_{R} = -21 \text{ kcals.,}$$

$CaO.SiO_2(l)$ referring here to the liquid in the supercooled state.

For the reaction,

$$2CaO_{(s)} + SiO_{2(s)} = 2CaO.SiO_{2(s)}$$

Richardson, Jeffes and Withers(54) give

$$\Delta G^{\circ}_{1773} = -30 \text{ kcals.,}$$

Fulton and Chipman(55) give

$$\Delta G^{\circ}_{1773} = -34.9 \text{ kcals.}$$

and the present work gives

$$\Delta G^{\circ}_{1773K} = -31.9 \text{ kcals., and}$$

$$\Delta G^{\circ}_{1773R} = -35.0 \text{ kcals.}$$

In conclusion therefore the free energy curves and values obtained from the present work agree within the limits of experimental error with most of the data given by other works, the agreement being best with the data of Fincham and Richardson(15).

(3) The $CaO-Al_2O_3-SiO_2$ System.

An attempt was made to calculate a_{SiO_2} from the a_{CaO} curves obtained experimentally. Since no $a_{Al_2O_3}$ values were known, the only method available was that of Wagner(56) which enables values of a_{SiO_2} to be calculated along lines of constant $N_{Al_2O_3}/N_{SiO_2}$ ratio by an adaptation of the Gibbs Duhem relation to ternaries.

Wagner showed that if $y = N_3/(N_3 + N_1)$,

$$\log a_1(N_2,y) = -y\int_{N_2^1}^{N_2} \frac{\partial}{\partial y}\left(\frac{\log a_2}{(1-N_2)^2}\right)_{N_2} dN_2 - \int_{N_2^1}^{N_2} \frac{N_2}{1-N_2}\, d\log a_2,$$

in which N_2^1 is the mole fraction of component 2 where $a_1 = 1$. Lines of constant y have $N_3/(N_3 + N_1) =$ constant, i.e., $N_3/N_1 =$ constant. In the present problem, component No.1 is SiO_2, No.2 is CaO, and No.3 is Al_2O_3. Therefore, the integration is carried out along joins of constant $N_{Al_2O_3}/N_{SiO_2}$ ratio. However, for the evaluation of the integration certain boundary conditions must be known. In this case, the choice of a standard state for SiO_2 is a slag in equilibrium with solid SiO_2. This restricts the use of Wagner's equation, since the integration can only be carried out along joins of constant $N_{Al_2O_3}/N_{SiO_2}$ ratio which intersect the SiO_2 liquidus at 1500°C, i.e., it restricts Wagner's equation to the area with $N_{Al_2O_3}/N_{SiO_2} \neq 7/93$, which is a very small part of the ternary. Wider application of Wagner's equation would, of course, be possible if the values of a_{SiO_2} were known along the 1500°C isothermal at which mullite separates out - but these values are not at present known. An attempt was made to apply Wagner's method to the present data in this restricted area, but it was found that the mathematics involved, especially in determining the first integral in the equation given above, were extremely complex,

and Wagner's method was therefore abandoned. Therefore, as this was the only method available, it was not possible to obtain accurate values of a_{SiO_2}.

By assuming that $a_{Al_2O_3}$ is constant along sections of constant $N_{Al_2O_3}$, and applying the binary Gibbs-Duhem relation along such a section, approximate values of a_{SiO_2} can be calculated. This method was used by Fulton and Chipman(55) to calculate a_{CaO} in $CaO-Al_2O_3-SiO_2$ slags from their values of a_{SiO_2}. The use of this method in the present work was limited to sections which cut the SiO_2 liquidus, i.e., with $N_{Al_2O_3} \not> 0.07$. It was, applied to the $N_{Al_2O_3} = 0.05$ section and the a_{SiO_2} curves shown on Fig.16 were obtained. Two points must be noted in connection with this method.

(1) Values of a_{CaO} along the $N_{Al_2O_3} = 0.05$ section are known only as far as $a_{CaO} = 0.0027$ at $N_{CaO} = 0.35$. Use of the Gibbs-Duhem relation demands a knowledge of the value of a_{CaO} at SiO_2 saturation. This was obtained by extrapolation of the Gibbs-Duhem N_{CaO}/N_{SiO_2} v. log γ_{CaO} graph, giving $a_{CaO} = 0.00054$ at SiO_2 saturation.

(2) The assumption that $a_{Al_2O_3}$ is constant along the $N_{Al_2O_3} = 0.05$ section is probably not correct, since the affinity of Al_2O_3 for CaO is considerably smaller than that of SiO_2 for CaO. One would therefore expect that, as N_{CaO} increased along the $N_{Al_2O_3} = 0.05$ section, $a_{Al_2O_3}$ would slowly decrease. The trend of a curve of constant $a_{Al_2O_3}$ is indicated in Fig.16. Therefore, the curves of constant a_{SiO_2} shown are probably nearer to the $CaO-SiO_2$ binary than they ought to be, i.e., they indicate minimum values for a_{SiO_2}.

Data obtained by other workers, with which the present work may be compared, is very limited. The conclusion of Holbrook and Joseph (57) can be compared qualitatively with the present work. In an attempt to find the factors controlling desulphurisation in the blast furnace, they carried out experiments using artificial $CaO-MgO-Al_2O_3-SiO_2$ slags, and found that, for MgO-free slags containing 30-50% SiO_2, 5-25% Al_2O_3 and 35-55% CaO, i.e., slags in the low-Al_2O_3 field of the $CaO-Al_2O_3-SiO_2$ ternary, the desulphurising power of the slags

(1) increased rapidly as lime replaced silica (by wt.),

(2) increased less rapidly as lime replaced alumina, and

(3) increased slowly as alumina replaced silica.

Since the desulphurising power of a slag corresponds to its lime activity, these conclusions may be compared with the results of the present work, as shown in Fig.15 and with the points emerging from the present work noted above (p. 79), and it can be seen that the present work completely confirms the conclusions of Holbrook and Joseph.

Hatch and Chipman(33) have carried out a very comprehensive series of experiments on $CaO-MgO-Al_2O_3-SiO_2$ slags in which they brought carbon-saturated iron into equilibrium with the slags, in order to obtain a better understanding of the physical chemistry of desulphurisation by blast furnace slags. They defined the desulphurising power of a slag as being equal to the ratio (% sulphur in slag)/(% sulphur in metal) and reached the following conclusions for slag compositions consisting of 30-50% CaO, 29-40% SiO_2, 6-27% Al_2O_3 and 0-19% MgO at 1500°C.

(1) The desulphurisation ratio (S)/[S] for slags containing approximately 1.5% S, is controlled by the excess base, where excess base is equal to $(CaO + \frac{2}{3} MgO) - (SiO_2 + Al_2O_3)$ in mols. per 100 gms. of slag.

(2) Alumina acts like silica in reducing the desulphurising power of a basic slag, in the more acid slags it is less harmful than silica.

(3) The sulphur concentration in the metal is not directly proportional to the sulphur in the slag, but, as the sulphur in the slag increases the desulphurising power (S)/[S] increases. This phenomena could not be explained by them with the data available.

Magnesia-free slags of the compositions used by Hatch and Chipman lie in the low-Al_2O_3 field of the $CaO-Al_2O_3-SiO_2$ ternary. Applying the above conclusions to MgO-free slags and comparing with the present work, it can be seen that conclusions(1) and (2) agree roughly with a_{CaO_K} curves in Fig.15, although in the present work, it has been shown that Al_2O_3 is less harmful than SiO_2 for slags of all basicities in the low-Al_2O_3 field. A possible explanation of the increase of (S)/[S] with increase in (S) is that $\gamma_{(S)}$ or $\gamma_{[S]}$ is not constant but varies with the sulphur content of the slag. It seems more probable that $\gamma_{(S)}$ in the slag decreases slightly as the sulphur content increases.

Chang and Derge(53) in a study of the reversible electrode potentials of molten $CaO-Al_2O_3-SiO_2$ slags, have given a graph of iso-e.m.f. curves at 1600°C. These iso-e.m.f. curves show one peculiarity, as Darken has pointed out in the discussion on this paper. If the cell is reversible then the iso-e.m.f. curves can, he points out, be interpreted as iso-activity curves. Also, the isothermal curves in the β-cristobalite

regions of the thermal equilibrium diagram are iso-activity curves. But whereas the isothermals slope upwards towards the SiO_2 corner, the iso-e.m.f. curves all slope down. It is clear that, if the cell is reversible, iso-e.m.f. curves must follow the direction of the iso-activity curves. The fact that they cross, according to Chang and Derge, must be attributed to the cell not being truly reversible, the use of the wrong chemical equation to express the reaction, or unusually large experimental errors. Whatever may be the reason, the results cannot be used for a comparison with the present work.

Fincham and Richardson(15) have calculated the sulphide capacities C_S, of $CaO-Al_2O_3-SiO_2$ slags at 1500°C and 1650°C from their experimental work on gas-slag equilibria. As was pointed out earlier, their sulphide capacity is equivalent to the function (S)/A of the present investigation, and to convert their sulphide capacities into activities (making the assumptions noted earlier) only requires the knowledge of the sulphide capacities of slags in equilibrium with solid CaO at the experimental temperatures. Unfortunately Fincham and Richardson have not carried out such experiments. Comparison with the present data can therefore only be made on the basis of the trend of the iso-C_S and iso-activity curves. This comparison shows that the curvature of the iso-C_S curves of Fincham and Richardson is considerably greater than that of the iso-activity curves of the present work - and this is true irrespective of whether the a_{CaO_K} or a_{CaO_R} curves are considered. However, Fincham and Richardson admit that they have an inadequate number of points from which to draw their curves accurately. The qualitative evidence of Holbrook and Joseph(57) and of Hatch and Chipman(33) given above also seems to support the slight

curvature of the iso-a_{CaO} curves given by the present work.

Fulton and Chipman(55) have obtained values of a_{SiO_2} at 1600°C in $CaO-Al_2O_3-SiO_2$ slags of up to 0.1 $N_{Al_2O_3}$ from investigations of slag-metal graphite reactions. From these values, they have calculated values of a_{CaO} by making the same assumption as has been made in the present work (viz., that $a_{Al_2O_3}$ is constant along lines of constant $N_{Al_2O_3}$) and using the Gibbs-Duhem binary relation. Their iso-activity curves have been shown on Fig.16. The slopes of their a_{SiO_2} curves are roughly the same as those of the present work, but their values are approximately half those of the present work, and yet, as has been pointed out, the values obtained in the present work are to be looked on as minimum values. As has already been stated, it may be that the discrepancy lies in the values of γ^{C}_{Si} in Fe-Si-C melts used by Fulton and Chipman.

Towers(58), from her investigations into the contact angles of slags on solid surfaces has given a value of $a_{SiO_2} = 0.15$ at 1520°C for a slag of 40% CaO, 40% SiO_2 and 20% Al_2O_3. This value has been plotted on Fig.16 and agrees roughly with the present work, this agreement being considerably better than that with the work of Fulton and Chipman.

It can be said, therefore, that the data presented here for a_{CaO} and a_{SiO_2} in $CaO-Al_2O_3-SiO_2$ slags at 1500°C is in general agreement with the small amount of data already published in this field.

CHAPTER VII.

GENERAL DISCUSSION AND CONCLUSIONS.

A study has been made by means of slag-gas experiments of the equilibrium in the reaction

$$(CaO) + \tfrac{1}{2}S_2 = (CaS) + \tfrac{1}{2}O_2$$

for which

$$K = \frac{(a_{CaS})}{(a_{CaO})} \left(\frac{P_{O_2}}{P_{S_2}}\right)^{\frac{1}{2}}$$

By making the assumption that γ_{CaS} does not vary with slag composition, the results of these experiments were used to determine a_{CaO} in $CaO-Al_2O_3$, $CaO-SiO_2$ and $CaO-Al_2O_3-SiO_2$ slags at 1500°C (as shown in Figs.11, 13 and 15). In the case of $CaO-Al_2O_3$ slags, a_{CaO} was obtained by comparing the sulphur pick-up with that of a slag of unit lime activity, using the same gas mixture. As it was necessary to use different gas mixtures in the case of $CaO-SiO_2$ and $CaO-Al_2O_3-SiO_2$ slags, a knowledge of the thermodynamic properties of the various sulphur compounds which might occur was required in order to calculate the composition of the gas at 1500°C. As experiments in which the same slag was equilibrated with different gas mixtures gave results which were found to agree best with the thermodynamic data of Kelley, these data were used in the calculation of a_{CaO} in $CaO-SiO_2$ and $CaO-Al_2O_3-SiO_2$ slags from the experimental results.

Fig.22 summarises the results obtained for a_{CaO} in $CaO-Al_2O_3$ and $CaO-SiO_2$ slags at 1500°C, and those calculated from the results of Fincham and Richardson(15) at higher temperatures. It will be seen that a_{CaO} is small for all compositions more acid than Ca_2SiO_4 but increases rapidly as N_{CaO} increases beyond that corresponding to Ca_2SiO_4.

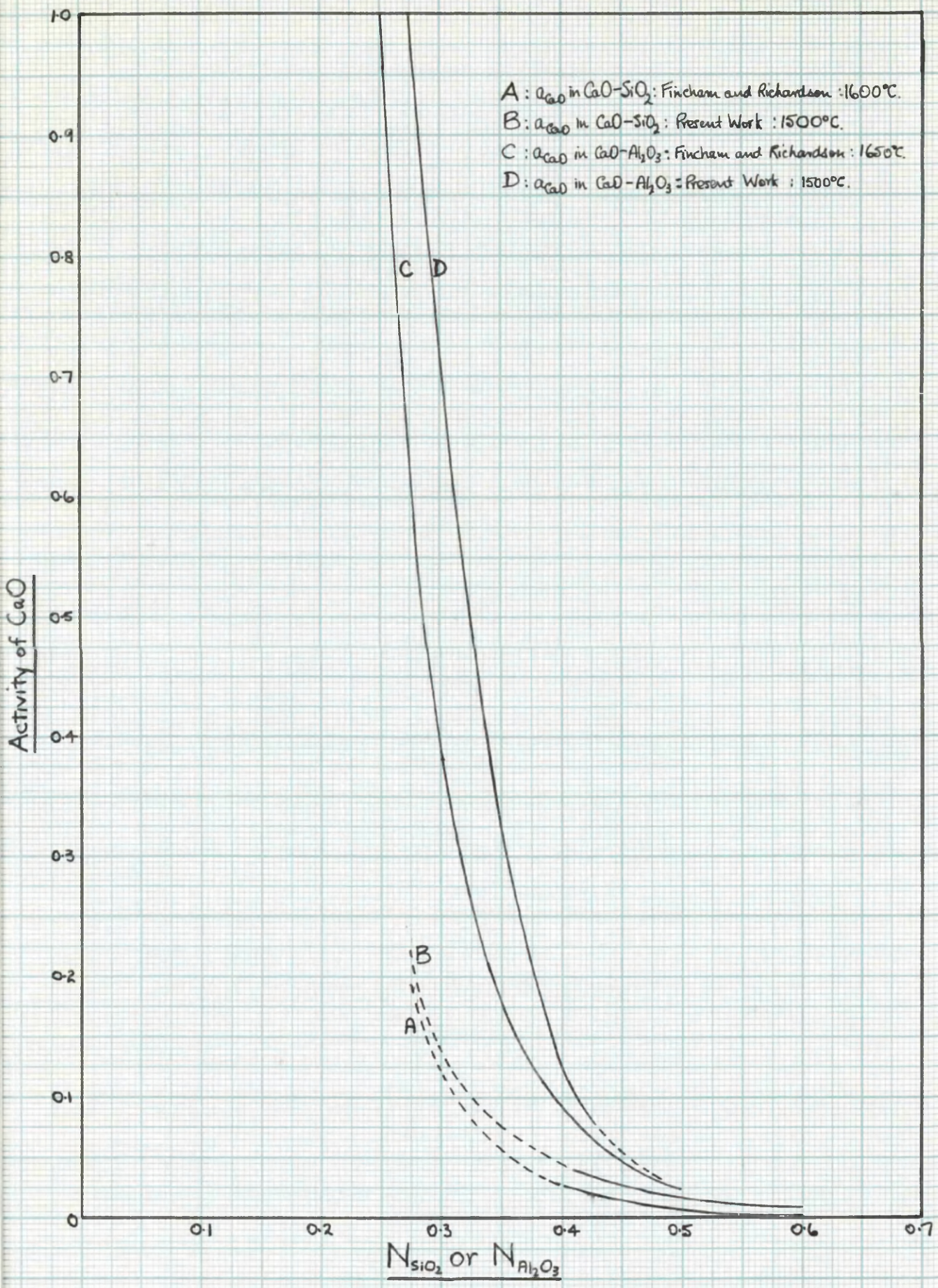


FIG 22 : ACTIVITY OF CaO IN $CaO-Al_2O_3$ AND $CaO-SiO_2$ SLAGS.

The effect of temperature appears to be comparatively small, only slight increases in N_{CaO} being required to produce the same values of a_{CaO} as the temperature rises. These observations are consistent with the oft-used method of interpreting slag behaviour in steelmaking slag-metal reactions by assuming the formation of Ca_2SiO_4 when calculating "base" or "oxygen-ion" activities. At lower basicities than that corresponding to Ca_2SiO_4, the desulphurising and dephosphorising powers of basic steelmaking slags are very poor. Fig.22 also shows that the corresponding rapid increase in a_{CaO} in $CaO-Al_2O_3$ slags occurs at much lower basicities and that the value of a_{CaO} is more temperature dependent. As somewhat similar behaviour might be expected in more complex slags, it would appear that the method frequently used of assessing the effect of Al_2O_3 on the base or oxygen ion activity by assuming the formation of $3CaO.Al_2O_3$, or AlO_3^{---} ions, is of dubious value.

It has been shown that the sulphur absorbed by the slag from a given gas mixture decreases with rise in temperature. High temperatures during melting and refining in open-hearth steelmaking should therefore result in lower metal sulphur contents. An increase in flame temperature, as would be obtained from a higher preheat, should have a similar effect. Increase in the oxygen potential of the gas phase, as would result from an increase in the air/gas ratio or improved combustion of the fuel should also minimise sulphur pick-up by the bath, or even cause loss of sulphur to the gas phase. On the other hand, excessive amounts of air might lead

to reduced flame temperatures which would offset to some extent the beneficial effects of increased oxygen potential. Similar considerations apply in the checkers where absorption of sulphur from the incoming fuel gas by lime and iron oxide dust deposited on the brickwork is favoured by the lower temperatures and reducing conditions prevailing on the ingoing side, and loss of sulphur to the waste gases during the subsequent reversal is favoured by the higher temperatures and oxidising conditions when the checkers are on waste gas.

Activities of lime in $CaO-Al_2O_3-SiO_2$ slags are of interest when considering slag-metal reactions in the blast furnace. The variation of a_{CaO} with slag composition has been given in Figs.15 and 17, from which it can be seen that:-

(a) in the "low-Al_2O_3" field, which covers the range of normal blast furnace slag compositions, a_{CaO} increases fairly rapidly with slag basicity, so that small composition changes may result in comparatively large changes in the sulphur content of the pig iron produced.

(b) slags in the "low-SiO_2" field have a_{CaO} values approximately 10-20 times those of normal blast furnace slags. They should give rise to very low metal sulphur contents, and, on account of the low a_{SiO_2} values of these slags low silicon contents should also be obtained. However, ores high in Al_2O_3 and low in SiO_2 (e.g., the West African Conakri ore) are comparatively rare and also present a number of practical difficulties in ore preparation and smelting.

The Gibbs-Duhem integration was used to calculate $a_{Al_2O_3}$ in $CaO-Al_2O_3$ slags and a_{SiO_2} in $CaO-SiO_2$ slags. It was also possible to estimate a_{SiO_2} in a limited portion of the $CaO-Al_2O_3-SiO_2$ diagram. No data has been published for the values of a_{CaO} and $a_{Al_2O_3}$ in $CaO-Al_2O_3$ slags but values calculated from the results of Fincham and Richardson were consistent with the present results. Similar consistency was obtained when the results for $CaO-SiO_2$ slags were compared with those of the latter workers at 1650°C. The present results differed considerably from those of Fulton and Chipman who used a rather lengthy extrapolation to obtain values of γ_{Si} in graphite-saturated iron to calculate a_{SiO_2}. It is probable that the values of γ_{Si} used were too low at the higher carbon (and lower silicon) contents.

The activity values obtained in $CaO-Al_2O_3$ and $CaO-SiO_2$ slags were used to construct free energy curves and to estimate the free energies of formation of $CaO.Al_2O_3$, 12 $CaO.7Al_2O_3$, $CaO.SiO_2$ and $2CaO.SiO_2$. The experimental results were not sufficiently complete to determine the free energies of formation of the ternary compounds $2CaO.Al_2O_3.SiO_2$ and $CaO.Al_2O_3.2SiO_2$. However, as the primary crystallisation fields of $2CaO.SiO_2$ and $2CaO.Al_2O_3.SiO_2$ have a common point at 1500°C for which $a_{Al_2O_3} \leqslant 1$, the free energy of formation of $2CaO.Al_2O_3.SiO_2$ must be considerably greater (numerically) than the value of -32 kcals obtained in the present work for $2CaO.SiO_2$.

APPENDIX:

Data Used in A_K and A_R v. Initial Gas Composition Graphs.

Calculation No.	Initial Gas Composition $\%SO_2$	Initial Gas Composition CO/CO_2	A_K	$-\log_{10}p_{O_2}$
Using Kelley's free energy equations, at 1500°C.				
1	0.77	1.470	321	7.890
2	0.80	1.473	330	"
3	0.83	1.475	339	"
4	0.86	1.478	348	"
5	0.89	1.480	357	"
6	0.92	1.483	366	"
7	0.77	1.514	336	7.914
8	0.80	1.517	346	"
9	0.83	1.519	355	"
10	0.86	1.522	364	"
11	0.89	1.525	373	"
12	0.92	1.527	383	"
13	0.77	1.557	351	7.938
14	0.80	1.560	361	"
15	0.83	1.563	371	"
16	0.86	1.566	381	"
17	0.89	1.569	391	"
18	0.92	1.572	401	"
19	0.77	1.601	367	7.960
20	0.80	1.604	377	"
21	0.83	1.607	387	"
22	0.86	1.610	397	"
23	0.89	1.613	407	"
24	0.92	1.616	417	"
25	0.50	1.01	112	7.585
26	1.00	1.03	204	"
27	1.50	1.05	282	"
28	2.00	1.07	353	"
29	0.50	1.83	335	8.085
30	1.00	1.89	546	"
31	1.50	1.96	720	"
32	2.00	2.04	858	"
33	0.50	2.60	537	8.381
34	1.00	2.72	845	"
35	1.50	2.86	1087	"
36	2.00	3.01	1294	"
37	0.50	3.32	712	8.585
38	1.00	3.51	1107	"
39	1.50	3.72	1416	"
40	2.00	3.95	1679	"

Calculation No.	Initial Gas Composition		A_K	$-\log_{10} P_{O_2}$
	$\%SO_2$	CO/CO_2		
41	2.00	3.57	1530	8.510
42	2.10	3.61	1570	"
43	2.20	3.65	1620	"
44	2.30	3.70	1660	"
45	2.40	3.74	1700	"
46	2.50	3.78	1740	"
47	2.00	3.71	1590	8.540
48	2.10	3.76	1630	"
49	2.20	3.80	1680	"
50	2.30	3.85	1720	"
51	2.40	3.89	1760	"
52	2.50	3.94	1810	"
53	2.80	3.28	1580	8.381
54	2.90	3.31	1610	"
55	3.00	3.35	1650	"
56	3.10	3.39	1680	"
57	3.20	3.43	1710	"
58	3.30	3.47	1740	"
59	2.80	3.43	1650	8.415
60	2.90	3.47	1680	"
61	3.00	3.52	1720	"
62	3.10	3.56	1750	"
63	3.20	3.60	1780	"
64	2.80	3.60	1720	8.448
65	2.90	3.64	1760	"
66	3.00	3.68	1790	"
67	3.10	3.73	1830	"
68	3.20	3.77	1860	"
69	2.70	3.72	1750	8.480
70	2.80	3.76	1790	"
71	2.90	3.81	1830	"
72	3.00	3.86	1870	"
73	3.10	3.91	1900	"
74	3.20	3.96	1940	"
75	3.30	4.01	1970	"
76	2.70	3.88	1820	8.510
77	2.80	3.93	1860	"
78	2.90	3.98	1900	"
79	3.00	4.03	1940	"
80	3.10	4.08	1970	"
81	3.20	4.13	2010	"
82	3.20	4.31	2080	"
83	3.30	4.38	2120	"
84	3.40	4.44	2160	"

Calculation No.	Initial Gas Composition		A_K	$-\log_{10}P_{O_2}$
	$\%SO_2$	CO/CO_2		
85	2.80	4.43	2060	8.594
86	2.90	4.50	2110	"
87	3.00	4.57	2150	8.594
88	3.10	4.63	2190	"
89	3.20	4.70	2230	"
90	3.30	4.77	2270	"
91	3.40	4.83	2310	"
92	2.70	4.73	2160	8.647
93	2.80	4.80	2200	"
94	2.90	4.87	2250	"
95	0.30	1.508	165	7.93
96	0.49	1.483	236	7.91
97	0.72	1.060	168	7.62
98	0.72	1.487	311	7.90
99	0.88	1.370	311	7.83
100	0.98	1.432	361	7.86
Using Richardson's free energy equations at 1500°C.				
			A_R	
101	0.77	1.552	180	7.938
102	0.80	1.554	186	"
103	0.83	1.557	192	"
104	0.86	1.560	198	"
105	0.89	1.562	204	"
106	0.92	1.565	210	"
107	0.77	1.510	171	7.914
108	0.80	1.512	177	"
109	0.83	1.514	183	"
110	0.86	1.516	189	"
111	0.89	1.519	195	"
112	0.92	1.521	201	"
113	0.77	1.469	160	7.890
114	0.80	1.471	166	"
115	0.83	1.473	172	"
116	0.86	1.474	178	"
117	0.89	1.476	183	"
118	0.92	1.478	189	"
119	2.90	3.39	1290	8.431
120	3.00	3.43	1320	"
121	3.10	3.46	1350	"
122	2.90	3.47	1320	8.448
123	3.00	3.51	1350	"
124	3.10	3.55	1390	"

Calculation No.	Initial Gas Composition $\%SO_2$	Initial Gas Composition CO/CO_2	A_R	$-\log_{10} p_{O_2}$
Using Richardson's free energy equations at 1500°C but replacing $\Delta G^\circ = -49{,}000 - 2.5T$ by $\Delta G^\circ = +6{,}000 - 2.5T$ for the reaction $S_2 + O_2 = 2SO$.				
125	0.81	1.52	316	
126	3.01	3.34	1630	
Using Kelley's free energy equations, at 1490°C and 1510°C.				
			A_K	Temperature.
127	0.85	1.518	317	1510°C
128	0.85	1.518	360	1500°C
129	0.84	1.524	410	1490°C
130	0.84	1.524	360	1500°C

Calculation based on the data of Fincham and Richardson(15) on the maximum sulphur content at saturation of a 41% CaO-52% Al_2O_3-7% SiO_2 slag at 1500°C - referred to on pp. 18-19;

Using an ingoing gas of

$$1\%\ SO_2,\ p_{N_2} = 0.5,\ p_{H_2}/p_{CO_2} = 3.25 \quad \ldots\ldots\ldots \quad (a)$$

for which they have calculated

$$p_{O_2} = 4.27 \times 10^{-10} \text{ and } p_{S_2} = 2.51 \times 10^{-4},$$

Fincham and Richardson obtained, using the above slag composition, a clear, glassy slag containing 1.26% S.

$$\therefore\ C_s = (\%S)(p_{O_2})^{\frac{1}{2}}/(p_{S_2})^{\frac{1}{2}} = 16.4 \times 10^{-4}$$

Using an ingoing gas of

$$2\%\ SO_2,\ p_{N_2} = 0.5,\ p_{H_2}/p_{CO_2} = 3.15 \quad \ldots\ldots\ldots \quad (b)$$

for which they have calculated

$$p_{O_2} = 7.08 \times 10^{-10} \quad \text{and} \quad p_{S_2} = 9.33 \times 10^{-4},$$

Fincham and Richardson obtained, using the same slag composition, a crystalline slag containing 4.2% S - which result they attribute to saturation with CaS.

Since C_s is constant for any given slag at a constant temperature, the value obtained above can be used to calculate the sulphur content which would have been obtained using the gas of composition (b), had not saturation intervened. The expected sulphur content thus calculated is

$$(\%S) = C_s \cdot (p_{S_2})^{\frac{1}{2}} / (p_{O_2})^{\frac{1}{2}}$$
$$= 16.4 \times 10^{-4} \times (7.08 \times 10^{-10})^{\frac{1}{2}} / (9.33 \times 10^{-4})^{\frac{1}{2}}$$
$$= 1.9\%$$

A C K N O W L E D G E M E N T S.

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